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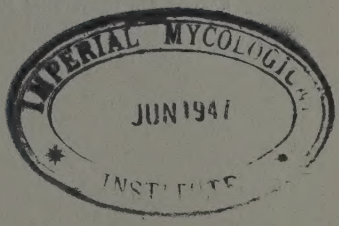
(DOKLADY)
DE L'ACADÉMIE DES SCIENCES DE L'URSS

NOUVELLE SÉRIE

1944



VOLUME XLV

№ 9

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NOUVELLE SÉRIE

12-me année

Paraissant tous les dix jours

1944

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Édition de l'Académie des Sciences de l'URSS
Moscou 1944

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1944. Volume XLV, № 9

MATHÉMATIQUES

SYSTÈMES COMPLETS DE BIVECTEURS

Par G. GOUREVITCH

(Présenté par A. N. Kolmogoroff, de l'Académie, le 9.III.1944)

Dans la présente Note on considère parmi les systèmes linéaires possibles de bivecteurs ceux que sont les plus simples en un certain sens, et pour les systèmes linéaires de ce type on donne une classification complète dans l'espace d'un nombre quelconque de dimensions.

Soit $\mathfrak{v}$ un système linéaire de bivecteurs; considérons l'ensemble $\mathfrak{A}$ de toutes les matrices A, ayant pour éléments A_i^x, telles que l'on a

$$\text{si } v_{ij} \in \mathfrak{v}, \quad \text{alors } A_{[i}^x v_{j]x} \in \mathfrak{v} \tag{1}$$

il est facile à voir que $\mathfrak{A}$ est une algèbre de Lie; elle s'appelle algèbre du système linéaire $\mathfrak{v}$.

Un système de bivecteurs $\mathfrak{v}$ est dit complet s'il est un système linéaire de bivecteurs dont l'algèbre est le normalisateur d'une certaine algèbre nulle complète $\mathfrak{P}$ (1). Une algèbre nulle $\mathfrak{P}$ définit une distribution des vecteurs de l'espace en échelons; choisissons dans l'espace un repère $p_1, p_2, \ldots, p_n$ de telle manière que les r_1 premiers vecteurs de ce repère appartiennent au 1-r échelon, les r_2 premiers vecteurs $(r_2 > r_1)$ au 2-d échelon, et ainsi de suite. Alors il est facile à voir que le bivecteur général v du système complet $\mathfrak{v}$ est de la forme

$$v = \sum \gamma_{ij} [p_i p_j], \qquad i > j; \qquad i, j = 1, 2, \ldots n \tag{2}$$

où les γ_{ij} sont des nombres ou bien nuls, ou bien tout à fait arbitraires, et $[p_i p_j]$ désigne le produit alterné des vecteurs p_i et p_j.

Introduisons pour les vecteurs du repère la notion de poids par rapport au système $\mathfrak{v}$. Le poids du vecteur p_i est égal au nombre des termes du second membre de (2) qui ne sont pas nuls et contiennent ce vecteur. Désignons par k_i le nombre des vecteurs du repère dont le poids est $\geqslant i$; alors le système des nombres $\boxed{k_1 k_2 k_3 \ldots}$ présente la caractéristique arithmétique du système complet. Pour abréger, dans le cas où parmi les nombres k_i il y a des nombres égaux, nous adopterons la notation avec des exposants; ainsi, par example, $\boxed{5^2 2^2}$ est la caractéristique arithmétique d'un système complet de bivecteurs dont le nombre des vecteurs de poids $\geqslant 2$ est égal à 5, le nombre des vecteurs dont le poids est égal à 4, est égal à 2, et il n'existe pas des vecteurs dont le poids surpasse 4.

Le résultat final de l'étude qui établit la classification de tous les systèmes complets de bivecteurs dans l'espace à un nombre quelconque de dimensions est le suivant.

Soit n le nombre de dimensions de l'espace; prenons un entier positif $s \leqslant {}^1/_2 n$ et choisissons $2s$ nombres arbitraires qui ne surpassent pas n:

$$a_1 > a_2 > \ldots > a_{s-1} > a_s > b_s > b_{s-1} > \ldots > b_2 > b_1 \qquad (3)$$

A chaque système de nombres de la forme (3) *et à un repère arbitraire de l'espace il correspond un système complet formé de bivecteurs*

$$v = \sum \gamma_{ij} [p_i p_j] \qquad i > j \qquad (4)$$

tel que dans chaque terme de la somme ou bien $i \leqslant a_1$, $j \leqslant b_1$, ou bien $i \leqslant a_2$, $j \leqslant b_2$, ou bien $i \leqslant a_s$, $j \leqslant b_s$, et tous les γ_{ij} sont des nombres arbitraires. Si nous formons tous les systèmes possibles de cette nature pour tous les $s \leqslant {}^1/_2 n$, et si nous y joignons le système formé du seul bivecteur $v = 0$, nous épuiserons ainsi tous les systèmes complets de bivecteurs de l'espace à n dimensions.

Il est évident que deux systèmes complets de bivecteurs correspondant à un même système de nombres (3), mais qui diffèrent l'un de l'autre par le choix des repères $p_1, p_2, \ldots, p_n$, peuvent être transformés l'un en l'autre par une transformation linéaire de l'espace; il est donc naturel de les considérer comme appartenant au même type. Il suit du théorème cité que le nombre de tous les types des systèmes complets de bivecteurs de l'espace à n dimensions est égal à $C_n^0 + C_n^{(2)} + \ldots + C^{z[n/2]}$, c'est-à-dire à 2^{n-1}.

La caractéristique arithmétique du système complet (4) est la suivante:

$$\boxed{a_1^{b_1} a_2^{b_2 - b_1}\, a_3^{b_3 - b_2} \ldots a_s^{b_s - b_{s-1}}\, b_s^{a_s - b_s - 1}\, b_{s-1}^{a_{s-1} - a_s}\, b_{s-2}^{a_{s-2} - a_{s-1}} \ldots b_1^{a_1 - a_2}} \qquad (5)$$

Il correspond au système complet (4) une algèbre nulle complète dont la caractéristique arithmétique est déterminée par les règles suivantes: si $a_1 < n$, $a_s - b_s > 1$, la caractéristique sera $\boxed{n a_1 \ldots a_s b_s b_{s-1} \ldots b_1}$. Si $a_1 = n$, $a_s - b_s > 1$, la caractéristique est de la forme $\boxed{a_1 \ldots a_s b_s b_{s-1} \ldots b_1}$. Et si $a_s - b_s = 1$, il faut omettre le nombre b_s dans les caractéristiques indiquées.

La somme de tous les nombres de la caractéristique arithmétique (5) est toujours un nombre pair. D'ailleurs, on a la règle suivante de complémentaire: à chaque type dont la caractéristique contient $a_1 = n$, il correspond un autre complémentaire dont la caractéristique contient $a_1 < n$, et qui jouit de la propriété suivante: si l'on place sous la caractéristique arithmétique du premier de ces types la caractéristique arithmétique du second écrite dans l'ordre inverse et si l'on fait l'addition, on obtient $\boxed{n^{n-1}}$ (c'est-à-dire le nombre n répété $n-1$ fois).

Manuscrit reçu
le 26. II. 1944.

LITTÉRATURE CITÉE

[1] G. B. Gourevitch, C. R. Acad. Sci. URSS, XLV, No. 2 (1944).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1944. Volume XLV, № 9

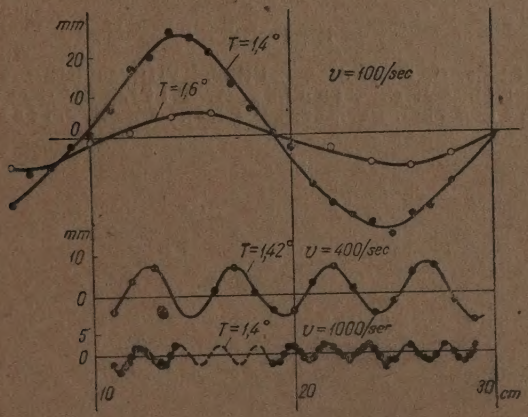
PHYSICS

SECOND SOUND IN HELIUM II

By V. P. PESHKOV

(Communicated by P. L. Kapitza, Member of the Academy, 2.X.1944)

In 1937 P. L. Kapitza (1) discovered the superfluidity, a property enjoyed by no other substance but helium II. The theoretical side of this phenomenon was investigated by Landau (2), who worked out a general quantum theory of liquid helium—the unique liquid existing at temperatures approaching absolute zero. According to this theory, helium II enjoys a number of unusual properties. It might be expected, for instance; that in helium II the propagation of the two following kinds of periodical movements is possible: the ordinary sound,



observed in 1938 by Findlay and others (3), which propagates in helium II at a rate of 230 m/sec.; and a second kind of sound whose speed is one order lower in magnitude.

Detailed computations made by Lifshitz (4) have shown that in the case of normal radiation by mechanical means sound II is masked by the ordinary sound. Contrary to this, a plane with periodically varying temperature mainly radiates sound II. Observations made with reference to temperature oscillations have also furnished evidence that is largely in favour of sound II.

The task of detecting this kind of sound in helium II experimentally was confided by P. L. Kapitza to the author.

By means of a sensitive set-up specially designed for the purpose I was indeed able to observe the waves predicted by Landau in helium II.

The waves were radiated by an alternating current which was passed through a heater made of a thin eureka wire. A bronze resistance thermometer served as indicator. It was connected in series to the secondary winding of a transformer and to a galvanometer shunted with a high capacity.

When an alternating current of the same frequency with the heat oscillations, *i. e.* twice the frequency of the current feeding the heater, was passed through the thermometer, the galvanometer indicated the presence of a direct current whose magnitude and sign varied according to the phase ratio between the oscillations of the temperature and the current.

In response to changing the position of the thermometer with respect to the heater, the detected current displayed periodical variations. This is shown by the adjoined figure in which distances from the heater are marked off as abscissae, and the ordinates are millimetres measuring the deflection of the galvanometer by the detected current. Above the λ point this phenomenon was not observed.

From experiments with the frequencies 100, 400 and 1000 periods per second the velocity of these waves in helium II at 1.4° C appears to be 19 ± 1 m/sec., as against 26 m/sec. which is the figure computed by Lifshitz.

The variation of the velocity with temperature corresponds in sign to the data yielded by the theory, but is greater in magnitude.

The quantitative study of these phenomenon is in progress.

The propagation of the Landau waves in helium II is a specific quantum property. As superconductivity is in many respects analogous to superfluidity; there is reason to surmise the existence of a similar phenomenon in superconductors when the temperature is such that the electronic specific heat and that of the lattice are magnitudes of the same order.

Institute of Physical Problems.
Academy of Sciences of the USSR.

Received
2. X. 1944.

REFERENCES

[1] P. L. Kapitza, C. R. Acad. Sci. URSS, XVIII, 28 (1937). [2] L. D. Landau, J. of Phys., 5, 71 (1941). [3] J. C. Findlay, A. Pitt, H. Grayson, Smith and J. O. Wilhelm, Phys. Rev., 54, 506 (1938). [4] E. M. Lifshitz, J. of Phys., VIII, 110 (1944).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1944. Volume XLV, № 9

PHYSICS

FLUORESCENCE OF ORGANIC DYE-STUFFS AS RELATED TO CHEMICAL CONSTITUTION

By P. P. FEOFILOV

(Communicated by S. I. Wawilow, Member of the Academy, 3.V.1944)

§ 1. One of the main unsettled questions of the fluorescence theory is how the constitution of molecules is related to their fluorescence ability. Following Meyer's attempt (1) to ascribe fluorescence to some definite groups of atoms (fluorophores), all work on this subject has been biassed by the desire to develop the fluorescence theory on similar lines with the classical chromophore theory. These attempts were concentrated on searching the structure formulae of fluorescent compounds for like atoms or like combinations of atoms, which, it was hoped; might prove to provoke fluorescence.

This trend of research has even found expression in the terminology which includes the definitions of batho- and hypso-flore groups as groups producing the shift of fluorescence in the long- and short-wave part of the spectrum; of auxoflores and diminoflores—groups stimulating or reducing the luminescence; *etc.*

This tendency to formal analogy may partly account for the relatively poor success of the theory treating the relation between chemical constitution and the fluorescence ability. Any fluorescent stuff is inevitably an absorbing one. Therefore it is only natural that some laws of the colour theory should be extended to fluorescence phenomena, though the analogy is rather trivial, and such notions as, for example, batho- and hypso-flore, which duplicate the notions of batho- and hypso-chrome groups in the theory of colour, do not seem to be very necessary, because in a vast majority of cases there is definite correspondence between absorption and fluorescence spectra. At the same time the basic notion of fluorophore remains extremely vague. From the investigation of spectral characteristics of luminescence and its polarization we are permitted to think that fluorophore, as a separate notion; is meaningless if a system in which luminescence takes place is implied.

This system is identical to the chromophore system of a molecule; since the absorption of light in the long-wave band responsible for the colour of the compound and the emitted radiation are both determined by the same electronic states of the molecule.

We can consider as fluorophoric such a configuration of the molecule; as a whole, or of its parts, that makes impossible for the energy of excitation to be converted into kinetic energy.

Thus, the question is not why a given compound is fluorescent, but rather why a compound that strongly absorbs light of some definite wave-lengths fails to re-emit it as fluorescence, with the result that the energy of the absorbed quantum is lost as optical energy *.

* A similar approach to the problem was made by Schmidt (2) as early as 1896, but up to now these ideas have not been sufficiently developed.

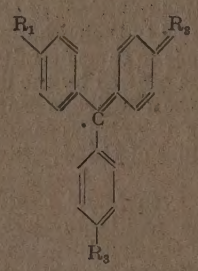
§ 2. The most typical structures of fluorescent dye-stuffs are known to be those including some definite aromatic or heterocyclic rings (Meyer's fluorophores) situated between two other aromatic rings. Light-emission phenomena arising upon the locking of theze rings have become classical examples of fluorescence [3,4].

So the formation of a bridge between benzene rings in representatives of a vast group of non-fluorescent triphenyl-methane dyes leads to the formation of a bright-fluorescent acridine, xanthene and other dyes.

A similar fluorogenic action was observed by the author upon the introduction of dye-stuffs of a certain chemical structure into their rigid solutions. It is known that many dye-stuffs become fluorescent in rigid solutions (in sugar, plastics, boric acid, *etc.*) and in the adsorbed state. The author observed this phenomenon with all dye-stuffs the structure of which admits of relative rotation of two large molecule-parts around the chain of conjugated double bonds responsible for the colour of the compound.

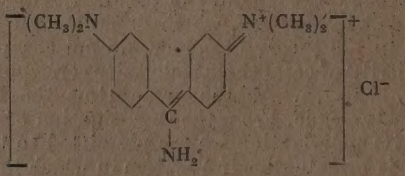
Thus, a bright fluorescence was observed when the following dye-stuffs were introduced into rigid sugar solutions.

Triphenyl-methane dyes of formula



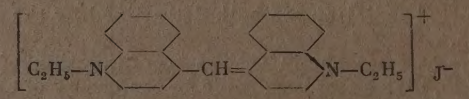
(fuchsine, crystal-violet, malachite green, rhoduline blue, alkaline phenol-phtaleine, aurine and many other basic and acid dyes).

Auramine, diphenyl-methane dye-stuff:

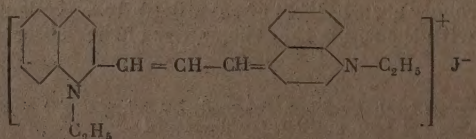


Cyanine-dyes:

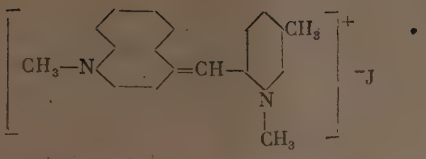
cyanine



dicyanine



pinaverdol



and many others.

The reason that may be put forward to account for the appearance of fluorescence ability in all these cases; is that some hindrance arises to preclude the relative rotation of benzene or chinoline rings around the connecting chain of conjugated double bonds.

In other words, the phenomenon may be interpreted on the basis of the hypothesis advanced by Forster* to explain the appearance of fluorescence in the case of a reversible polymerization of some cyanine dyes observed by Jelley([5]) and Scheibe ([6]).

The analysis of the electronic states of the ethylene bond ([7]) shows that in a basic state the stable configuration of a molecule is one with plane arrangement of the radicals.

Contrary to this, the first excited state, attained as a result of absorption in the basic band, has an energy minimum when the arrangement of the planes in which single bonds are lying, is perpendicular**.

Rotation around conjugated bonds in the dye-stuff molecule likewise encounters a strong barrier in the fact that resonance between the basic structures of the molecule stabilizes the latter towards such a rotation. It may be supposed that just as in the case of a simple ethylene bond the stable configuration of the excited dye-stuff molecule differs from that of a molecule in the basic state. If the stable basic state is that with plane arrangement of rings, the excited molecule has the minimum energy when the rings have perpendicular (or, in general, any other) orientation. Thus, the excited molecule will show a certain tendency to a relative turn of the rings.

Only when such a turn is impossible on account of structure or external hindrances (the presence of locking bridges, rigidity of the solution; adsorption, formation of compact polymers, *etc.*), will the molecule retain the excitation energy in the form of optical energy and be able to emit it after a while as fluorescence. If it is possible for the molecule to turn in this way, the disactivation of the perpendicular excited state is either not accompanied by radiation at all, or is realized as far infra-red radiation. The remaining energy excess is lost by the molecule when it returns from the «perpendicular» to the plane state. The energy set free by the relative rotation of parts of the excited molecule is several tens of times as great as that of the heat movement, so that the appearance of fluorescence in rigid solutions is observed with viscosities considerably exceeding those necessary to hinder the Brownian movement of the molecule (which can be detected from the depolarization of fluorescence ***).

Adsorption of the dye-stuff molecules on the surface of solid bodies also frequently leads to the appearance of fluorescence ability. As, however, every adsorption cannot preclude the possibility of the above-mentioned rotations, the fluorescence due to absorption is a less frequent phenomenon than that following the introduction of molecules into rigid solutions.

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* Not published, cited after Scheibe ([6]).

** This is known to explain the conversion of fumaric acid into maleic, and conversely, by exposure to ultra-violet rays, as well as many other cases of photo-chemical cis-trans-conversions. The plane configuration of an excited molecule proves to be unstable, the relative term of the radical is realized and the excited cis-trans-isomeres become indiscernible. Return to basic state leads to an unstable «perpendicular» configuration passing with certain probability either into a cis- or trans-form.

*** It is of great interest to obtain quantitative data on the viscosity at which the fluorescence makes its appearance.

The introduction of the dye-stuff into a rigid solution does not essentially change the electronic system of the molecule. Therefore, unlike the cases where the fluorescence appears as a result of the formation of a bridge between benzene or chinolene rings; the colour of the compound does not diminish in depth—the absorption spectrum practically displays no shift.

The processes discussed here seem to be a frequent but undoubtedly not the unique cause of the conversion of excitation energy into heat energy, and account for the lack of fluorescence ability in a many intensely coloured organic compounds.

State Optical Institute.

Received
30. IV. 1944.

REFERENCES

[1] R. Meyer, ZS. phys. Chem., **24**, 468 (1897). [2] G. Schmidt, Ann. d. Phys., **58**, 103 (1896). [3] J. Formánek, Untersuchung und Nachweis org. Farbstoffe auf spektr. Wege, 1, Berlin, 1908, SS. 73. [4] H. Ley, Fluoreszenz and chem. Konstitution, Hdb. d. Phys., **21**, 710 (1929). [5] . E. Jelley, Nature. **139**. 631 (1937). [6] G. Scheibe, ZS. f. Elektrochem.. **47**, 73 (1941). [7] R. Mulliken, Phys. Rev., **41**, 751 (1942).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1944. Volume XLV, № 9

GEOPHYSICS

ON THE DIURNAL VARIATIONS OF TEMPERATURE IN THE SURFACE LAYER OF THE SEA AND ON HEAT CURRENTS AT THE SEA—AIR INTERFACE

By S. V. DOBROKLONSKY

(Communicated by A. N. Kolmogoroff, Member of the Academy, 25.III.1944)

Generally the surface layer of the sea in not very high latitudes displays diurnal variations of temperature which are connected with the absorption of solar radiation by water.

Observations made in the temperate and equatorial zones of the open sea, in the Gulf of Trieste and in South Kattegat show the temperature of the sea surface to oscillate within 0.3—0.9° C in a course of 24 hours. The time of maximum temperature at the sea surface lags behind the solar noon by as much as 2—4 hours on the average (1).

Still wider variations of temperature were observed by K. V. Shutilov in the summer of 1938 in the littoral zone of the Black Sea. The range of oscillations varied from 0.8 to 3.0° C, according to the day of observation (2). The phase difference between the maximum of solar radiation and that of sea surface temperature varied within as broad a range as 1 to 5 hours.

The factors determining the temperature distribution in the surface layer with reference to space and time appear to be as follows. First, the flow of solar radiation converted into heat throughout the thickness of the water; secondly, the amount of the turbulent heat exchange between the various layers of the sea; and, thirdly, the exchange of heat through the interface between sea and air. The latter, obviously, includes the exchange by means of long-wave radiation which, in view of the strong absorption of long waves (above 2—3 μ) by water; we assume to take place from the surface; the exchange by convection; and the exchange connected with the processes of evaporation and condensation.

The author has made an attempt

1) to describe the diurnal variations of temperature in the surface layer mathematically, taking into account that the solar radiation is absorbed continuously as it penetrates into the volume of water;

2) to develop a method for the calculation of the flow of heat across the sea—air interface.

It is mainly because the latter is variable with meteorological conditions that there are differences in phase displacement between solar radiation and the surface temperature of the sea.

In determining the constants, use will be made of sea temperature observations and of actinometric data on the magnitude of solar radiation and the character of its penetration into the volume of water.

In the case of a cloudless sky the flow I_0 of solar radiation (both direct and diffuse), penetrating into the sea across 1 cm^2 of its horizontal surface, is sufficiently

symmetrical with respect to the local noon and can be expressed as a Fourier series composed entirely of cosines

$$I_0 = J_0 + J_1 \cos \alpha t + J_2 \cos 2\alpha t + J_3 \cos 3\alpha t + \ldots \quad (1)$$

where $\alpha = 2/\pi T$, and T is equal to 24 hours.

The paths of the rays between the sea surface and any other horizontal plane separated from it by a distance z, as measured along the vertical; are different in so far as they depend upon the angle of incidence ζ.

On account of refraction, however, they are confined within rather narrow limits — from 1.52 z for $\zeta = 90°$ to 1.00 z for $\zeta = 0°$.

For simplicity we shall suppose the total flow to propagate along the vertical.

At a depth z we have

$$I = I_0 e^{-mz} \quad (2)$$

where m is a coefficient that allows for the average extinction of radiation.

Examining the heat balance of an elementary volume (in the absence of horizontal heat transfer) on the basis of (1) and (2) leads to the differential equation

$$c\delta \frac{\partial \vartheta}{\partial t} - k \frac{\partial^2 \vartheta}{\partial z^2} = mJ_0 e^{-mz} + mJ_1 e^{-mz} \cos \alpha t +$$

$$+ mJ_2 e^{-mz} \cos 2\alpha t + mJ_3 e^{-mz} \cos 3\alpha t + \ldots \quad (3)$$

in which c and δ are specific heat and density of the sea water, respectively; ϑ is temperature; k is coefficient of turbulent heat conductance, taken to be invariable with the depth, because the layer in which the processes unde consideration take place is several meters thick

The boundary conditions for settled oscillations are given as:

1) Temperature at the sea surface

$$\vartheta|_{z=0} = \vartheta_0 + \sum_{n=1}^{\infty} \theta_n \cos(n\alpha t - \psi_n) = \vartheta_0 + \sum_{n=1}^{\infty} (\theta'_n \cos n\alpha t + \theta''_n \sin n\alpha t). \quad (4)$$

2) Gradient of mean diurnal temperature at a depth z_0, at which the temperature run can lawfully assumed to be linear because the absorption of radiation has here practically no influence:

$$\frac{\partial \vartheta}{\partial z}\Big|_{z=z_0} = \bar{G} \quad (5)$$

The general solution (3) then takes the form

$$\vartheta = \vartheta_0 + Gz + \frac{J_0}{km}(1 - e^{-mz}) - \sum_{n=1}^{\infty} \frac{mJ_n e^{-mz}}{\sqrt{n^2c^2\delta^2\alpha^2 + k^2m^4}} \cos(n\alpha t + \varphi_n) +$$

$$+ \sum_{n=1}^{\infty} A_n e^{-\beta_n z} \cos(n\alpha t - \beta_n z + \gamma_n) \quad (6)$$

where

$$\cos \varphi_n = \frac{km^2}{\sqrt{n^2c^2\delta^2\alpha^2 + k^2m^4}}; \qquad \sin \varphi_n = \frac{nc\delta\alpha}{\sqrt{n^2c^2\delta^2\alpha^2 + k^2m^4}} \quad (7)$$

and

$$\beta_n = \sqrt{\frac{nc\delta\alpha}{2k}} = \sqrt{\frac{n\pi c\delta}{kT}} \quad (8)$$

and the constants A_n and γ_n are:

$$A_n = \sqrt{\theta_n^2 + J_n'^2 + 2\theta_n J_n' \cos(\psi_n + \varphi_n)} = \\ = \sqrt{\theta_n'^2 + \theta_n''^2 + J_n'^2 + 2J_n'(\theta_n' \cos\varphi_n - \theta_n'' \sin\varphi_n)} \quad (9)$$

$$\operatorname{tg}\gamma_n = \frac{\theta_n \sin\psi_n - J_n' \sin\varphi_n}{\theta_n \cos\psi_n + J_n' \cos\varphi_n} = \frac{\theta_n'' - J_n' \sin\varphi_n}{\theta_n' + J_n' \cos\varphi_n} \quad (10)$$

In (9) and (10) for brevity sake there is adopted the notation

$$\frac{mJ_n}{\sqrt{n^2c^2\delta^2\alpha^2 + k^2m^4}} = J_n' \quad (11)$$

The flow of heat through the sea surface, if the direction «downward» be defined to be positive, is

$$Q = -k\frac{\partial\vartheta}{\partial z}\Big|_{z=0} = -J_0 - kG - \sum_{n=1}^{\infty} \frac{km^2 J_n}{\sqrt{n^2c^2\delta^2\alpha^2 + k^2m^4}} \cos(n\alpha t + \varphi_n) + \\ + \sum_{n=1}^{\infty} A_n k\beta_n \sqrt{2} \cos\left(n\alpha t - \gamma_n + \frac{\pi}{4}\right) \quad (12)$$

Obviously, it can also be written in the form

$$Q = Q_0 + \sum_{n=1}^{\infty} (Q_n' \cos n\alpha t + Q_n'' \sin n\alpha t) \quad (13)$$

where

$$Q_0 = -J_0 - kG \quad (14)$$

$$Q_n' = -\frac{J_n}{\sqrt{1 + \frac{n^2c^2\delta^2\alpha^2}{k^2m^4}}} \cos\varphi_n + A_n k\beta_n \sqrt{2} \cos\left(\gamma_n - \frac{\pi}{4}\right) \quad (15)$$

$$Q_n'' = +\frac{J_n}{\sqrt{1 + \frac{n^2c^2\delta^2\alpha^2}{k^2m^4}}} \sin\varphi_n - A_n k\beta_n \sqrt{2} \cos\left(\gamma_n + \frac{\pi}{4}\right) \quad (16)$$

From the expressions obtained for the temperature of the sea and the flow of heat through the sea surface we are permitted to make certain conclusions:

1. The mean diurnal temperature of the sea, as given by the first three terms of the expressions (6), when $G < 0$, which is the ordinary case in summer, is a maximum not at the surface, but at a certain depth $z = L$, where

$$L = -\frac{\lg\left(-\frac{kG}{J_0}\right)}{m \lg e} \quad (17)$$

By means of this relation k can be determined from observational data.

2. The temperature wave in the surface layer obeys a more complicated law of propagation than in the case of the ordinarily adopted superficial absorption of solar radiation (3). It also affords the means for determining k.

3. The constant portion of flow of heat and the amplitude of the harmonics in its variable portion are not, generally speaking, equal to zero.

4. By taking m to be large (the absorption of the radiation by the surface) and confining ourselves to the first harmonic, we shal simplify the amplitudes of the variable portion:

$$\left.\begin{aligned} Q_1' &= -J_1 + \theta_1 k\beta_1 \sqrt{2} \cos\left(\psi_1 - \frac{\pi}{4}\right) \\ Q_1'' &= -\theta_1 k\beta_1 \sqrt{2} \cos\left(\psi_1 + \frac{\pi}{4}\right) \end{aligned}\right\} \quad (18)$$

For $Q_1' = 0$ and $Q_1'' = 0$ it follows from (18) that $\psi_1 = \frac{\pi}{4} = 3$ hours.

$$J_1 = \theta_1 k \beta_1 \sqrt{2} \tag{19}$$

The relation (19) is identical with that used by Shutilov in computing k [2].

It evidently cannot be used (with m large) unless direct computations of the variable portions of the heat flow components will show them to be small in comparison with J_1.

The formulae we had obtained were used by us in evaluating the heat flow for the diurnal cycle of sea temperature observations carried out by Shutilov at the Black Sea hydrophysical station on August 11—12, 1938. On that day the phase displacement ψ_1 reached the exceptionally high value of ~ 5 hours. The curve of the mean diurnal temperature (see figure) has a

Mean diurnal temperature distribution along the vertical

characteristic run with a maximum under the surface, which is in accordance with the theory.

Computation shows that:

1) the amplitude of the heat flow is 70 to 80 per cent of the solar radiation amplitude, and the flow attains its maximum at 9 p. m.;

2) the amplitude of the heat flow has the same order of magnitude with the maximum loss of heat by evaporation during the day which varies with the velocity of wind and deficiency of moisture.

From these results we are permitted to think that in the case considered water vapour in quantities nearly equal to those evaporated during the day was condensed at the sea surface after sunset.

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Received
25. III. 1944.

REFERENCES

[1] A. Defant u. O. v. Schubert, Veröffentlichungen des Instituts for Meereskunde, H. 25 (1934). [2] K. V. Shutilov, Bull. Acad. Sci. URSS, sér. géograph. et géophys., No. 4—, 447 (1941). [3] В. В. Шулейкин, Физика моря, 1941, стр. 293.

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1944. Volume XLV, № 9

GEOPHYSICS

COSMIC DUST ACCORDING TO ACTINOMETRIC MEASUREMENTS

By N. N. KALITIN

(Communicated by B. G. Fessenkow, Member of the Academy, 9.III.1944)

It has long since been pointed out by the Swiss actinometrist C. Dorno [1] that, according to observations carried out at Davos, a several per cent decrease in the Sun radiation intensity is observable in August, which should, to his opinion, be associated with the group of shooting stars, the «Perseids».

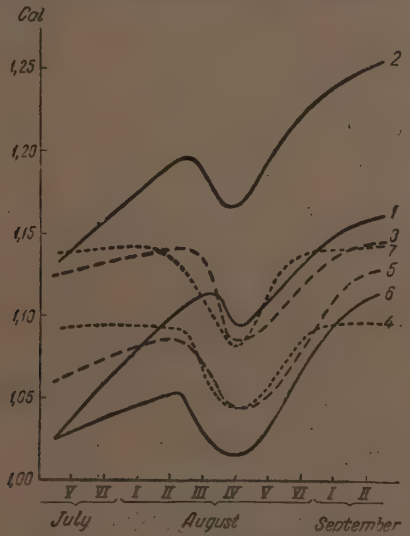


Fig. 1. Sun radiation intensity for each 5 days for a Sun height of 30°. *1*, Pavlovsk; *2*, Yakutsk; *3*, Tashkent; *4*, Tbilissi; *5*, Kursk; *6*, Rostov/Don; *7*, Samarkand

Wide-scale actinometric measurements have uninterruptedly been carried on in this country for several decades. Owing to these measurements, one can not only attempt to determine the existence of this minimum, but also to measure its magnitude and inquire into the cause to which it is due.

For solving this problem several places have been chosen, where actinometric observations were carried on during a considerable number of years, and the observational data were available to the author. These places were: Pavlovsk, observations carried out for 25 years (1913—1937); Yakutsk, 12 years (1931—1942); Tashkent, 12 years (1926—1937); Tbilissi, 10 years (1928—1937); Kursk, 8 years

(1928—1935); Rostov/Don, 8 years (1930—1937); Samarkand, 7 years (1931—1937).

For Sun heights of 30°, and in some points of 41.8°, the mean values of Sun radiation intensity were calculated for each five days, beginning with the fifth 5-day period of July and ending with the second 5-day period of September. The values obtained have been reduced to the mean distance between the Sun and the Earth.

Fig. 1, which is plotted on the basis of the data of Table 1, illustrates the variation in the magnitude of the Sun radiation intensity.

Table 1

Average Intensity of Sun Radiation for 5-Day Periods* (in calories)

		July		August						September		Number of observations
		V	VI	I	II	III	IV	V	VI	I	II	
For Sun heights of 30°												
Yakutsk	I	1.14	1.15	1.17	1.21	1.18	1.16	1.20	1.22	1.23	1.26	203
	n	18	24	15	25	30	24	1.71	17	17	16	
Pavlovsk	I	1.04	1.05	1.07	1.09	1.12	1.10	1.11	1.13	1.15	1.16	663
	n	84	86	58	80	73	64	50	69	54	45	
Kursk	I	1.00	1.08	1.09	1.08	1.07	1.04	1.05	1.09	1.15	1.12	197
	n	16	19	19	25	20	19	20	21	25	13	
Rostov/Don	I	1.05	1.02	1.06	1.06	1.02	1.01	1.03	1.07	1.11	1.12	374
	n	36	45	33	35	28	30	44	43	38	42	
Tbilissi	I	1.14	1.08	1.09	1.10	1.06	1.05	1.04	1.10	1.10	1.09	394
	n	23	43	37	43	29	45	33	50	45	46	
Tashkent	I	1.13	1.13	1.13	1.14	1.15	1.07	1.10	1.10	1.15	1.14	920
	n	89	96	90	90	92	90	90	112	86	85	
Samarkand	I	1.14	1.14	1.15	1.13	1.12	1.07	1.15	1.12	1.14	1.14	531
	n	54	62	57	51	55	52	52	60	43	45	
For Sun heights of 41.8°												
Rostov/Don	I	1.17	1.15	1.18	1.16	1.17	1.13	1.16	1.18	1.21	1.23	363
	n	35	39	35	31	27	30	44	45	40	37	
Tbilissi	I	1.25	1.20	1.20	1.21	1.19	1.17	1.18	1.21	1.22	1.22	431
	n	27	45	45	46	32	51	34	56	47	48	
Tashkent	I	1.22	1.23	1.13	1.22	1.24	1.18	1.20	1.20	1.23	1.22	916
	n	87	93	91	95	94	87	86	109	91	83	
Samarkand	I	1.13	1.24	1.25	1.23	1.23	1.19	1.26	1.22	1.24	1.24	529
	n	57	59	56	53	54	52	50	60	42	46	

* In this table and in what follows Angströms' scale is used to express the magnitudes of Sun radiation intensity.

In Table 1 I denotes the Sun radiation intensity for normal surfaces; n is the number of observations made to obtain the mean for five days.

For the places for which many observations are available, the scattering of the points is not particularly great (Pavlovsk, Yakutsk), and the minimum of radiation is sharply expressed.

For all the other places; curves characterizing the changes in the radiation can also be constructed with a certainty.

From Table 1 and Fig. 1 it may clearly be seen that there exists a rather sharp minimum for all the seven places, amounting to several per cent and corresponding to one and the same period, *viz.* the fourth 5-day period of August. The simultaneousness of its occurrence for all the places, the same order of its magnitude, irrespective of the different climatic conditions prevailing at the places of observations and the distance they lie apart (thus, for instance, the distance between Yakutsk and Tbilissi is 5600 km), all this is evidence that the cause responsible for this minimum is of the same origin in all cases, and that it is independent of the Earth.

To obtain the average minimum curve, magnitudes of the radiation observed in all the places for every 5-days were taken from Table 1 and on the basis of the latter average values for Sun heights of 30 and 41.8° were calculated. These means are summarized in Table 2 and Fig. 2.

Table 2

Average Values of Sun Radiation Intensity for 5-Day Periods (in calories)

	July		August						September		Number of observations
	V	VI	I	II	III	IV	V	VI	I	II	
For Sun heights of 30°	1.090	1.099	1.108	1.114	1.101	1.076	1.094	1.121	1.138	1.145	3282
For Sur heights of 41.8°	1.205	1.208	1.210	1.211	1.197	1.170	1.183	1.211	1.223	1.226	2239

The curves of Fig. 2 permit to form an idea as to the nature of the causes responsible for the radiation minimum.

Let us analyse the upper curve obtained from the greater part of observations (3282). The dotted line represents the course of the radiation as it would be in case there were no causes for its decrease. The duration of the decrease in the transparen-

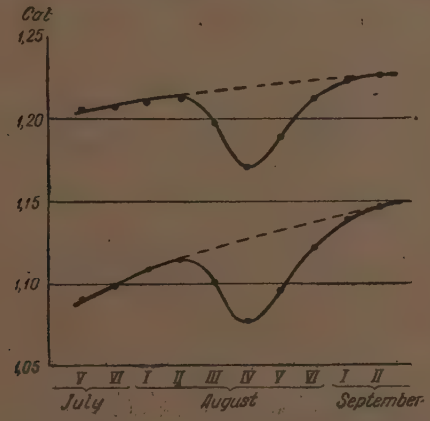


Fig. 2. Average Sun radiation insensity for each 5 days for a Sun height of 30° (bottom curve) and 41.8° (top curve)

cy makes up about 27 days. The drop in the transparency continues for 10 days and its rise for 17 days.

The decrease in the intensity of the Sun radiation is apparently associated with the passing of the «Perseids». Towards the 8th of August the Earth enters into an accumulation of cosmic dust which reaches its utmost density when the Earth comes to its position of the 18th of August; on September the 5th the Earth leaves this accumulation of dust.

Putting the average velocity of the Earth's motion in its orbit equal to 29.77 km/sec., we obtain for the diameter of the dust accumulation a figure of the order of 70 million km, the absorbing mass being distributed unequally. The maximum of absorption is observed at a distance of 26 million km from the starting point; the second part of the accumulation is of a higher density.

The reduction in the intensity of Sun radiation due to the presence of cosmic dust may proceed in either of the following two ways: in its course the Earth may,

on the one hand, directly enter into the dust accumulation which will absorb a part of the radiation; the dust accumulation can also lie between the Earth and the Sun. On the other hand, dust may accumulate also in the upper layers of the atmosphere, being a product of the combustion of the shooting stars. But the latter fact is not likely to play any important part.

It is quite possible that the decrease in the Sun radiation caused by the accumulation of cosmic dust is enhanced by the dust present in the upper layers of the atmosphere as a product of combustion of the meteorites.

For a more detailed analysis of the phenomenon described, an examination of larger series of measurements of Sun radiation intensity is necessary; the main absorber of Sun radiation in the atmosphere being water vapour, it is preferable to make measurements of the short-wave part rather than the integral flow of radiation.

From a preliminary analysis of the data available for Sun radiation intensity it may be inferred that its minimum is likely to occur during the third 5-day period of April; when it is associated with the stream of «Lyrids».

As far back as in 1925, when studying the annual course of the atmosphere transparency for Pavlovsk ([3]); attention was paid to the fact that in April a lower coefficient of atmosphere transparency is observed than it might be anticipated from the values of its annual course; but no explanation of the phenomenon could then be found.

If the results of the measurements of Sun radiation intensity made in different parts of the globe are compared, the actinometrical method permits to record not only the periodic cases where the Earth enters the accumulations of cosmic dust, but also the sporadic cases, as has previously been predicted by the author([3]).

The fluctuations observed in the value of the Sun constant may possibly be explained by the sporadic decrease in the Sun radiation due to cosmic dust. An analysis of the Sun constant value considered from this point of view would be extremely desirable.

It is quite probable that in the course of astrophotometrical work certain corrections will have to be introduced, based on the data on the transparency fluctuations obtained from measurements of Sun radiation intensity.

Received
9. IV.1944

REFERENCES

[1] C. Dorno, Tägliche, jährliche und seculäre Schwankungen der Sonnenstrahlung in Davos, Rapport fait à la Conférence internationale de la lumière, Lausanne, 1928. [2] Н. Н. Калитин, Изв. Гл. физич. обсерватории, № 1 (1920). [3] Н. Н. Калитин, Геофизич. сборник, IV, вып 3(1925).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1944. Volume XLV, № 9

PHYSICAL CHEMISTRY

THE ELECTROCHEMICAL BEHAVIOUR OF STAINLESS STEELS

III. THE CHANGE IN THE ELECTRODE POTENTIALS OF STAINLESS STEELS AFTER ABRASION UNDER SOLUTION

By G. V. AKIMOV, Corresponding Member of the Academy, and G. B. CLARK

Elsewhere (1) we showed that the chemical stability of stainless steels is explained by the presence of a protective film.

In the present work our goal was a determination of the ability of diverse stainless steels to restore the protective film after injury, by measuring the electrode potential before abrasion and during abrasion and the change in the electrode potential after abrasion. By comparing the curve for the time variations of the electrode potential after abrasion with the values of the potential before abrasion, one may gain an idea of the rate of restoration of the protective film on the steel in a given solution.

The measurements were carried out in four typical media: 3 per cent NaCl, 0.1 *N* HCl, 0.1 *N* HNO_3 and 0.1 *N* NaOH, in air. The composition and treatment of the steels has been described elsewhere (1). Except in special cases, the state of the surface was identical for all samples (treatment included polishing, washing, drying at room temperature and storage in desiccator for at least 24 hours).

We repeat the nominal composition in per cent of the investigated steels: [1] 17 Cr, [2] 30 Cr, [3] 19 Cr, 9 Mn, [4] 8 Cr, 17 Mn, [5] 17 Cr, 7 Mn, 3 Ni, [6] 18 Cr, 8 Ni, [7] 18 Cr, 8 Ni, 3 Mo.

A graphical analysis of the experimental results is given in the accompanying figure. In the 3 per cent NaCl solution the electrode potentials for all steels after abrasion change in the positive direction, which points to the restoration of the protective film.

In the first place it should be noted that this process proceeds rather slowly. For steel 18-8 [6], for example, the potential returns to its initial value (before abrasion) approximately after 20 min. For steel 17 Cr [1] the initial value is reached approximately after an hour. Only curves for steels [1] and [6] have been given in the diagram. The curves for the other steels look exactly the same and occupy positions in between the two given ones. The curves for steels [2] and [7] are very close to one another.

Sections of the curves up to one hour are given in the diagram. The experiments usually lasted up to 2.5—4 hours, and in a number of cases up to 20—30 hours.

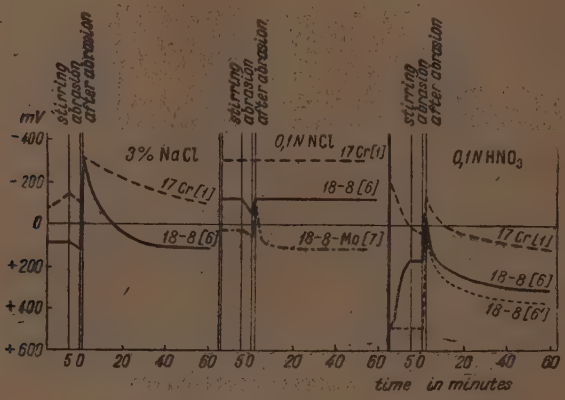
However, this protraction of the time of an experiment did not reveal anything new. The small increase in the nobility of the potential (25—50 mV) after stirring began may be explained by fresh portions of solution containing oxygen from the air being brought into play. In the 0.1 *N* HCl solution all the steels, with the exception of steel [7], corroded. The character of the curve of the electrode potential also points to this. Abrasion does not alter the value of the electrode potential for steels [1], [3], [4], and [5]. For steels [2] and [6] a slight decrease in

nobility is observed in comparison with somewhat of an increase in nobility after stirring begins.

For all steels, with the exception of [7], the potential after abrasion does not increase.

Steel 18-8 with 3 per cent Mo [7] gives a unique type of curve in this solution. Abrasion noticeably decreases the nobility of the surface of this steel (by 100—150 mV).

However, after abrasion has been discontinued, the potential rapidly returns to its initial value (before abrasion), which points to the extremely high ability of steel containing molybdenum to restore the protective film even in a solution of HCl; *i. e.* in the presence of such powerful activators as Cl^--ions and H^+-ions.



The change in the electrode potentials of stainless steels in typical media after abrasion under solution

Interesting peculiarities in the electrochemical behaviour of steels are revealed by the electrode potential curves in the 0.1 *N* HNO_3 solution. Here all the investigated steels may be divided into two groups. Under the first fall steels [1], [3], [4] and [5]. The initial values of the potential for these steels are quite negative (—150, —200 mV), rather rapidly becoming more positive until they reach a value in the neighbourhood of 0 mV. After abrasion there is a rather rapid increase in nobility of the potential; which soon becomes 200—300 mV more positive than its initial value.

Thus; the abraded surface of these steels is rendered passive especially energetically in nitric acid.

The other group is comprised of the steels 2, 6, and 7. These steels show an extremely positive initial potential (about + 500 mV), but decrease in nobility in the 0.1 *N* HNO_3 solution. Thus, this value of the potential proves to be unstable in the given conditions. A decrease in nobility takes place to + 200, + 100 mV. Abrasion decreases the nobility of these steels by approximately the same amount as those in the first group, *i. e.* by 100—200 mV. After abrasion has been discontinued; a rapid increase in nobility of the potential; *i. e.* restoration of the film, takes place; nevertheless the potential even after 4—5 hours does not attain its high initial value and becomes stable approximately at + 300 mV.

In our previous communications ([1]; [2]) we pointed out that the electrode potentials of steel 18-8 in a solution of nitric acid depend upon the state of the surface. The solid curve in the figure is for steel 18-8 [6], treated according to the procedure adopted in the present investigation (polishing, washing, drying at room temperature and storage in a desiccator for at least 24 hours). The dotted curve 18-8 [6']

is for a sample of the same steel that was treated differently—pickled in 5 *N* HCl, washed and kept for 3 hours at 100—150° C. It is seen that the stability of the protective film in this case has markedly increased. The potential retains its high initial value (+500 mV) right up until abrasion. Abrasion decreases the nobility of the potential to the same value as in the case of steel 18-8 treated by the standard procedure.

The curve after abrasion for the sample 18-8 [6′] lies approximately 100 mV more positive than that for sample 18-8 [6].

In the 0.1 *N* NaOH solution all the steels behave similarly, namely, the initial value of the electrode potential is restored very rapidly after abrasion. Thus, the investigation has shown that in the majority of the media studied the stainless steels restore the ruptured protective film. Moreover, the rate of restoration is not great and depends upon the composition; treatment and state of the surface of the steel.

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Received 17. I. 1944.

REFERENCES

[1] G. V. Akimov and G. B. Clark, C. R. Acad. Sci. URSS, XLIII, No. 7 (1944).
[2] G. V. Akimov and V. P. Batrakov, ibid., XLV, No. 3 (1944).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1944. Volume XLV, № 9

PHYSICAL CHEMISTRY

THE RAMAN SPECTRA OF SOME SULPHUR CONTAINING COMPOUNDS

By R. E. CHERNITSKAYA and J. K. SYRKIN,
Corresponding Member of the Academy

This work is concerned with a study of the Raman spectra of β-dioxydithioethylene, phenylthiourea, diphenylthiourea, dithioethylene and thiourea. The following frequency values were obtained for:

1) β-dioxydithioethylene .

Obtained by oxidizing dithioethylene with hydrogen peroxide. Recrystallized from 50 per cent alcohol. Photographed in a 15 per cent solution of chloroform.

$\Delta\nu = 333(1)$, 405(2), 424(1), 467(1), 497(0), 514(3), 590(1), 610(1), 1033(4), 1113(1), 1142(1), 2846(1), 2924(2), 2968(2), 3029(2), 3049(2).

2) Phenylthiourea $SC\begin{matrix}NH_2\\NHC_6H_5\end{matrix}$ (Kahlbaum).

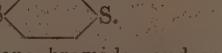
Recrystallized twice from alcohol. M. P. = 146° C. Photographed in a 20 per cent solution of dioxane.

$\Delta\nu = 487(2)$, 1074(1), 1105(1), 1496(1), 1510(1), 1550(1), 1596(1), 1606(2), 1674(1), 1725(1), 2152(0), 2453(0), 3045(1), 3117(1).

3) Diphenylthiourea $SC\begin{matrix}NHC_6H_5\\NHC_6H_5\end{matrix}$ (Becker).

Recrystallized twice from alcohol. M. P. = 153° C. Photographed in a 15 per cent solution of dioxane.

$\Delta\nu = 486(2)$, 1085(2), 1195(1), 1404(2), 1514(1), 1594(3), 1604(1), 1674(1), 1765(2), 1840(1), 2137(1), 3050(1), 3130(1), 3208(1).

4) Dithioethylene  .

Obtained from ethylene bromide and sodium sulphide. Recrystallized from alcohol. M. P. = 111 — 111.5° C. Photographed in a 25 per cent solution of carbon tetrachloride.

$\Delta\nu = 276(0)$, 631(3), 648(0), 696(0), 942(0), 1003(1), 1118(0), 1210(0), 1404(1), 2908(3), 2947(4).

5) Thiourea $SC\begin{matrix}NH_2\\NH_2\end{matrix}$ (Kahlbaum).

Recrystallized twice from alcohol. M. P. = 172 — 174.5° C. Photographed in a 12 per cent aqueous solution.

$\Delta\nu = 356(0)$, 420(3), 487(1), 620(3), 671(1), 732(5b), 1099(3), 1400(1), 1647(1), 1832(1), 2014(1), 2104(1).

It would not be without interest to pick out in the spectra obtained the frequencies of the vibrations characteristic of the C=S and S=O bonds.

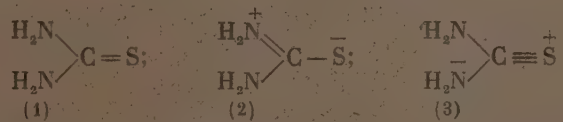
Ordinarily, the frequencies of double bonds, for example, the C=C, C=N and C=O, are characteristic frequencies. They are observed in the spectra of all the compounds of a given class. Moreover, the frequency, as a rule, changes quite insignificantly in value upon transition from one compound to another.

This situation is much more complicated with regard to the C=S frequency. We know the vibration frequency of the CS molecule (1), equal to 1285 cm^{-1}. Just as in the CO molecule, here apparently the C=S, $C \equiv S$ and $\overset{+}{C}-\overset{-}{S}$ states are represented.

By analogy with the frequency of the carbonyl bond, which, as is known, is considerably less than the vibration frequency of carbon monoxide, one may expect the value for the frequency of the C=S bond in thiourea and its derivatives, if found, to lie below 1285 cm^{-1}.

In the carbonyl bond, as distinct from the CO molecule, only the $\rangle C=O$ and $\rangle \overset{+}{C}-\overset{-}{O}$ states are represented. By analogy, the $\rangle C=S$ and $\rangle \overset{+}{C}-\overset{-}{S}$ states are represented in thiourea.

In compounds resembling thiourea, the following structures are possible:



(1) (2) (3)

Similar structures are represented in urea, too. Experiment shows that the frequency of the C=O bond in urea is equal to 1655 cm^{-1}, *i. e.* considerably less than the frequency of the C=O bond in acetone, equal to 1708 cm^{-1}. This may be explained by the considerable predominance of structure (2) with an ordinary bond over structure (3). The ability of sulphur to give sulphonium compounds in which the sulphur forms three covalent bonds and carries a positive charge, is well known. Sulphur gives sulphonium compounds easier than oxygen gives oxonium compounds.

There is evidence to the fact that frequencies in the neighbourhood of 1100 cm^{-1} are observed in compounds with a C=S bond.

Thus, in thiourea we find the frequency 1099 cm^{-1}; in phenylthiourea; 1074 and 1105 cm^{-1}; in diphenylthiourea; 1085 cm^{-1}, and in thioacetamide, 1044 cm^{-1} (2).

However, this does not mean that this frequency can be taken at its face value to indicate the presence of a C=S bond. A number of compounds are known that do not contain a C=S bond, but still have frequencies in their spectra that are close to 1100 cm^{-1}. Such, for example, are the deformation frequencies of the NH_2-group. Such lines are observed in hydrazine; in compounds of the type H_2N—COOR, *etc.*, where there is no C=S bond; in general.

On the other hand, frequencies in the neighbourhood of 1100 cm^{-1} have been found in the spectra of a number of molecules that do not contain aminogroups, but have a C=S bond.

Thus, in the spectrum of thiophosgene, $CSCl_2$ (3), the line 1121 cm^{-1} referring to the symmetrical valence vibration has been found, and in tetramethylthiourea, $CS[N(CH_3)_2]_2$ (4), the frequencies 1058 and 1094 cm^{-1}.

All this is indicative that a single-valued solution of the problem is rendered difficult. It is quite probable, nevertheless, that the frequency in the neighbourhood of 1100 cm^{-1} is connected with the presence of a $\rangle C=S$ group.

As for compounds containing an ordinary C—S bond, the lines 635, 655, 960, 1045 and 1150 cm^{-1} are ordinarily found in the corresponding spectra. In the spectrum of dithioethylene we found the frequencies 631; 648, 942 and (1118) cm^{-1}. In the spectrum of β-dioxydithioethylene we found the frequencies 610 and 1033 cm^{-1} and the weak lines 1113 and 1142 cm^{-1}.

It should be noted that in the spectrum of the SO_2 molecule in the gaseous state the most intensive line has a frequency equal to 1150 cm^{-1}, while in the spectrum of the $O=SCl_2$ molecule the frequency 1299 refers to the symmetrical valence vibration ([5]).

We find lines with a frequency close to 1200 cm^{-1} in different sulphur compounds containing the $\rangle \overset{+}{S}=\overset{-}{O}$ bond. However, it should be noted that the number of now known spectra of compounds containing short C=S and C=O bonds is still too small to refer them definitely to this frequency.

Of the spectra we investigated; those for dithioethylene and thiourea had been studied before by Medard ([6]) and by Edsall ([7]), and Kohlrausch and Wagner ([2]), respectively.

Except for the very weak line 557 cm^{-1} and the line 817 cm^{-1} of medium intensity, which we did not detect, Medard's data for the spectrum of dithioethylene coincide with ours.

The spectrum of thiourea was photographed by Edsall in an aqueous solution, and by Kohlrausch and Wagner in the crystalline state. We found a far greater number of lines than Edsall. The spectrum obtained by Kohlrausch and Wagner is richer in lines and does not coincide completely with ours; evidently owing to the fact that their data are for the substance in the solid state. However, the lines of greatest intensity are reproduced in both works:

Our data: 487, 732, 1099, 1400.

Kohlrausch and Wagner's data: 483, 735, 1094, 1374.

It is interesting to note that the frequencies of the N—H bond do not appear in the spectra of thiourea in aqueous solution that were obtained both by us and by Edsall; whereas they are represented by lines of considerable intensity in the spectrum of thiourea in the solid form obtained by Kohlrausch and Wagner.

Also of notable interest is the relatively weak intensity of all our spectra, for example, that of dithioethylene; in which the most intensive line, 631 (S); referred to the CCl_4 intensity scale (in which the line 313 is taken as 100); amounts to all in all 5 units.

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Received
8.IX. 1944.

REFERENCES

[1] W. Jevons, Proc. Roy. Soc., London, A, **117**, 351 (1928); F. H. Crawford and W. A. Shureliff, Phys. Rev., **43**, 766 (1933); **45**, 860 (1934). [2] K. W. F. Kohlrausch and J. Wagner, Z. phys. Chem., B, **45**, 229 (1940). [3] J. H. Hibben, The Raman Effect and its Chemical Applications, N. Y., 1939, p. 401. [4] K. W. F. Kohlrausch and A. Pongratz, Monatsh., **70**, 226 (1937). [5] F. Matossi and H. Aderhold, Z. Physik, **68**, 683 (1931); Venkateswaran, Indian Journ. Physik, **6**, 275 (1935). [6] L. Medard, Journ. Chim. Phys., **33**, 626 (1936). [7] J. T. Edsall, Journ. Phys. Chem., **41**, 1 (1937).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1944; Volume XLV, № 9

GEOCHEMISTRY

ON SOME CASES OF FORMATION OF DISPERSE GOLD SEGREGATIONS IN IRON SULPHIDES

By I. MASLENITSKY

(Communicated by S. S. Smirnov, Member of the Academy, 15.III.1944)

It was a fact well-known to those engaged in concentrating and dressing gold ores that there are such resistant gold-bearing pyrites as defy gold extraction either by amalgamation or cyanization. This refractory nature of pyrites can hardly find a correct interpretation unless we are to assume the presence of highly-disperse inclusions of gold or of gold compounds within the mass of pyrite.

Aside from its practical importance; the problem as to the nature of the inclusions of gold and its association with pyrite is of great scientific interest for the geochemical interpretation of the primary gold-ore and gold-bearing polymetallic deposits.

The mode of the association of gold with pyrite and other sulphides can be established by the mineragraphic method on natural objects. The mineragraphic method, however, has one essential drawback—the casual nature of the inclusions observed; for it is practically impossible to examine a sufficient number of polished sections that would run into very high figures (1). Therefore the mineragrapher is in some cases liable to make a mistake by ascribing a general character to a casual form observed. Without rejecting the use of mineragraphy as a method, the author thinks it more correct to apply to the study of the shape and nature of internal inclusions of gold the method of synthesis of gold-bearing sulphides of iron and of the pure sulphide of gold.

1. Synthetic Gold-Bearing Pyrite. For obtaining pyrite and studying the form of segregation of gold in it, under conditions of iron oxides or salts acted upon by sulphur emanations at a temperature of ~400° C, the author had recourse to the method of pyrite synthesis as proposed by Weller.

By selecting the optimum proportions of the components and temperature conditions, the author succeeded in obtaining a large number of large crystals of pyrite of a high degree of perfection. The formation under the conditions of our experiment of an artificial mineral identical with the natural pyrite has been confirmed by chemical, mineragraphic and X-ray analyses. By adding in the course of synthesis of the mass under reaction gold in the form of auric chloride or of colloidal gold it was possible to obtain pyrite with a varying content of gold.

All the large gold particles formed in the process of synthesis, as well as the external segregations of gold on the faces of pyrite crystals were removed by precision gravity separation and amalgamation.

The most thorough examination under the microscope of a large number of polished sections with a magnification ~1200 revealed in the residue only some isolated inclusions of gold 1—2μ in size, which could not account for the high gold content of synthetic pyrite (~300 g/t).

This is evidence of the submicroscopic state of the ground mass of gold in synthetic pyrite. The high dispersedness of gold in pyrite has also been confirmed by chemical and special mineragraphic studies.

Chemical investigations have shown that only negligible amounts of gold are recovered from the pyrite with the aid of mercury and cyanide solutions, notwithstanding a very fine reduction of the pyrite, the use of oxidants and a prolonged contact with the solvents. Upon the disintegration of the pyrite by strong acids, however, only disperse gold in the shape of an amorphous brown powder was found in the residue.

In order to reveal submicroscopic gold by the mineralogical method, use was made of preliminary heating of polished sections (2). As a result a more or less intense coalescence of the submicroscopic particles of gold into layer aggregates, according to the temperature and duration of the heating, can easily be seen under the microscope.

The examination of polished sections of crystals of gold-bearing pyrite has shown that as a result of heating at 600° the pyrite is completely or partly

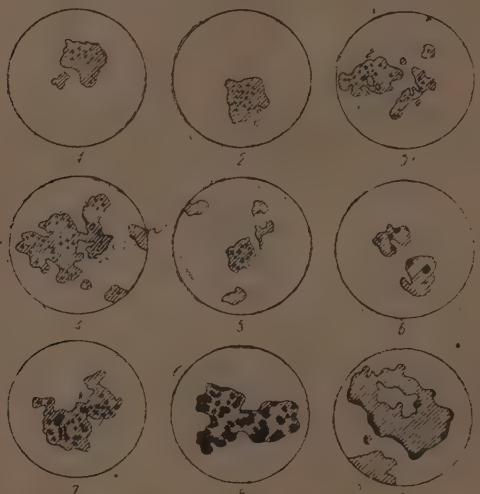

Fig. 1. Submicroscopic gold in synthetic pyrite as revealed by thermal methods. Dashed grains, pyrite and pyrrhotine. Black inclusions and borders, metallic gold.

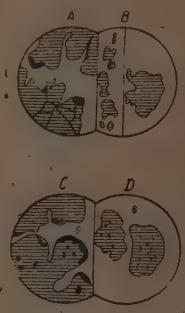

Fig. 2. Microdrawings of gold inclusions in natural and synthetic pyrite. *A*, *B*, gold inclusions in pyrites from California (Sherwood). *C*, *D*, gold segregations in synthetic pyrite (Maslenitsky); *p*, pyrite. *a*, quartz

transformed into pyrrhotine. In the pyrite subjected to heating the number of gold segregations recorded under the microscope has been found to be considerable—from 20 to 70 gold particles per polished section.

These segregations of gold are of a different nature (Fig. 1). In some of the pyrite crystals gold was observed in the shape of small internal inclusions; in crystals subjected to a more intense heating it was found in the shape of internal drop-like inclusions and as films on the surface of the crystals.

Noteworthy is the close resemblance of the external shape of the gold segregations in pyrites from California recorded by Sherwood (3) to the gold segregations observed in synthetic pyrite by the present author (Fig. 2). This points to how difficult it is to form a clear idea as to the sequence of pyrite and gold segregation from data of mineragraphical analysis alone. We feel inclined to believe that the occurrence of gold segregations on the surface of the pyrite crystals is not always evidence of a later deposition of gold from the solutions.

2. Solubility of Gold in Synthetic Gold-Bearing Pyrrhotine. Gold and iron were fused in equivalent amounts under excess of sulphur, supplied through slag under pressure (after MacLaurin) (4). Upon cooling it was found that the bulk of the gold had deposited on the bottom of the crucible, which points to a sparing solubility of gold in iron sulphide under the physical-chemical conditions of the experiment. However, the layer of macroscopically homogeneous ferrous sulphide contained 1.97 per cent gold.

As shown by mineragraphic analysis, the sulphide, formed as a result of the fusion, consisted largely of typical pyrrhotine. Under the microscope gold was observed in the form of films on the surface of pyrrhotine crystals, spherical and drop-like inclusions within sulphide grains and point-like disperse (<0.5 μ) inclusions inside the pyrrhotine crystals.

Upon the removal of the gold particles and films by the above described method, the pyrrhotine was found to contain ~ 0.5 per cent gold, in the form of submicroscopic and highly disperse (~ 0.5 μ) internal inclusions which could not be recovered by cyanide solutions. These results reveal a degree of dispersion of gold in iron sulphide approaching the state of solid solution.

In the gold-bearing alloys of iron sulphides obtained, along with gold inclusions, inclusions of a pinkish and light-grey colour were also observed under the microscope. The occurrence of these bright light-coloured inclusions made us think of the existence of gold sulphide under the conditions of fusion at a high pressure of sulphur; at elevated temperatures and a lower pressure of sulphur this sulphide of gold is unstable.

3. Synthesis of Gold Sulphide. A brownish powder of gold sulphide prepared by precipitation at a temperature of $+8°$ C was subjected to heating at 160—165° C under a pressure of 5000 kg/cm². A compact lustrous product of a lead-grey colour was obtained, splitting along perfect planes. Chemical analysis showed 78.85 and 78.99 per cent gold, and 18.82 and 19.90 per cent sulphur, which corresponds to the formula Au_2S_3.

The mineragraphic analysis showed the synthetic product to consist mainly of a quite individualized compound with the following constants:

Colour light, cream-grey; against PbS, light-grey; against ZnS, greyish-white; against Au, grey.

Hardness above 2, below 3. Anisotropic to polarized light.

Etching: HCl, H_2SO_4 concentrated and 1 : 1, negative. HNO_3 concentrated, when acted upon by vapour becomes brown. HNO_3 1 : 1, negative. $AgNO_3$, becomes slightly brown, coating removable, after which gold is revealed. KCN, becomes slightly brown, the coating may be removed revealing pale gold.

Under the microscope, in the sulphide grains white and pink inclusions and small (1—2 μ) inclusions of metallic gold are observable.

At usual temperature the sulphide is resistant to acids, being decomposed by cyanide solutions. When heated above 200° C it is decomposed under segregation of gold, first in the form of specks and minute «segregations», a continuous aggregate of gold segregations of irregular shape being subsequently formed.

4. Disperse Gold Inclusions in Natural Pyrite. The experimental work which has been carried out explains the causes of formation of internal submicroscopic gold inclusions in some pyrites.

It may be assumed that when the deposits were formed, in some cases at a temperature of about 400° C and at an elevated pressure of sulphur, melts-solutions of iron sulphides could have been formed, containing sulphides of other metals, inclusive of gold. Upon a decrease of temperature and pressure a crystallization and separation of pyrite from such metals took place, as well as a decomposition of gold sulphides. In the process of pyrite crystallization, gold as an element with a lattice of a different size would, according to the conditions of cooling, either be retained inside the pyrite grains in the shape of disperse inclusions, or squeezed out to the surface of the crystals and deposited there in the form of films.

Conclusions

1. Experiments on the synthesis of gold sulphide and gold-bearing iron sulphides have shown that the pyrite and pyrrhotine formed at a temperature of about 400° C can possibly include measurable quantities of finely disperse and submicroscopic gold, not detectable under the microscope even at high magnifications.

2. The submicroscopic gold may in some cases be represented by the product of decomposition of primary Au_2S_3 in iron sulphides. This gold content of pyrite and pyrrhotine is due to the conditions of formation and of the subsequent cooling.

3. The form of the gold separated out from pyrite in the author's experiments corresponds to the forms of natural gold encountered in the pyrites of certain deposits.

Received
8. III. 1944.

REFERENCES

[1] И. Н. Масленицкий, Золотая промышленность, № 4—5 (1939); Цветные металлы, № 8 (1942); Форма и ассоциация золота с минералами в сульфидных рудах цветных металлов, Л., 1940. [2] G. Bürg, Metall und Erz, H. 13, 332 (1930). [3] В. Линдгрен, Месторождения золота и платины, 1932. [4] J. S. Mac Laurin, J. Chem. Soc. (London), **69**, 1269 (1896).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
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GEOLOGY

MINERALOGICAL CORRELATIVES OF KUNGURIAN DEPOSITS OF THE NEAR-URAL REGION OF BASHKIRIA

By S. G. SARKISSIAN

(Communicated by P. I. Stepanov, Member of the Academy, 20.III.1944)

Kungurian deposits are widespread in the near-Ural region. Facially they are highly variable and are represented by different lithological varieties. The problem of a stratigraphical subdivision of Kungurian deposits is of a great scientific and practical importance. The guide fauna of Kungurian deposits is comparatively scarce, and there are places where it is altogether lacking; therefore all the methods of geological science available should naturally be used to inquire into the stratigraphy of the Kungurian deposits and the possibility of a large scale correlation to be drawn. One of these methods is afforded by correlative mineralogy which has successfully solved a number of similar problems over the territory of the near-Ural area of Bashkiria.

The mineralogical investigations carried out by the author aimed at finding the composition of heavy terrigenous minerals, and thus to make possible the subdivision of Kungurian deposits by the methods of correlative mineralogy.

Specimens of cores and slime from holes of the Western massif, the Kuzminovsky, Termen-Elga and Allakaevo regions of the Ishimbay area were investigated.

Among the heavy terrigeneous minerals, the author* discovered grains of almandine, tourmaline, rutile, common hornblende, zircon; rarely, diopside, epidote, and still more rarely picotite; a great many ore minerals were also found, among which pyrite predominated. In spite of the scarcity of the mineral species found, it is possible to establish some regular relationship in their distribution throughout the section.

In the operated area of the Ishimbay oil field stratigraphically below the Ufa deposits the so-called transitional formation is usually distinguished; it is represented by an interbedding of clays, marls and sandstones, highly gypsiferous, with rare intercalations of anhydrite and gypsum. The mineralogical composition of the transitional formation is represented either by a pyroxene-hornblende, or by a garnet association. The former characterizes the lower part of the Ufa series, the latter the upper part of the Kungurian stage. Thus, it is correct to attribute no stratigraphical value to the transitional formation. In this case the question presents itself, whether the transitional formation should be referred to the lower portion of the Ufa series, or to the upper portion of the Kungurian. The mineralogical methods make it possible to trace a distinct boundary between the Ufa and the Kungurian deposits; on the basis of the data of mineralogical analysis, a part of

* In the mineralogical investigations the author was assisted by N. D. Pokrovskaya.

the transitional formation should therefore necessarily be assigned to the Kungurian, and another part, to the Ufa series. This conclusion will be the most correct, for if use be made of lithological evidence and great importance attached to the «red beds», occurring within the transitional formation, the latter should be referred to the lower part of the Ufa series. If the guiding rôle be ascribed to the hydrochemical conditions of the basin, and in the case discussed to the presence of

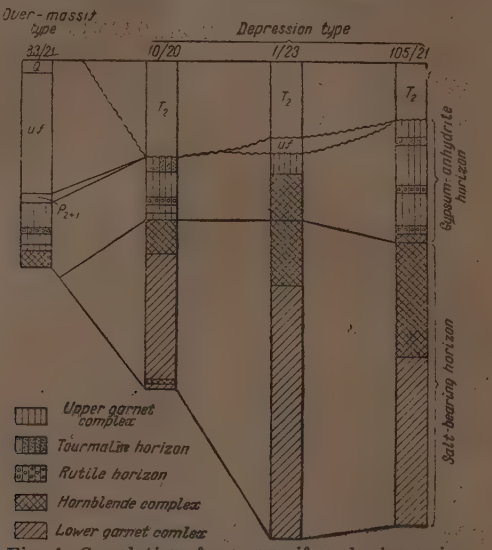

Fig. 1. Correlation of over-massif and depression types of the Kungurian according to the terrigenous minerals. Scale 1 : 10000

intercalations of gypsum and anhydrite and the total sulphatization of the rocks of the transitional formation, the latter is to be considered as the upper horizons of the Kungurian. It should be borne in mind that the conditions of sedimentation in relict, somewhat freshened basins existed in the lower portion of the Ufa series and occasionally in its upper horizons as well. So, in this particular case, the nature of the basin can scarcely be of any material import. It would possibly be more correct to consider the upper part of the transitional formation for which a pyroxene-hornblende association is characteristic, as a new stage in the life of the Lower Permian, and to assign it to the lower portion of the Ufa series. The transitional formation, represented by the garnet association, usually enriched with gypsum and anhydrite, would be the final cycle in the life of the Kungurian basin and may be referred to the upper portion of the Kungurian.

The stratigraphical scheme of Kungurian deposits traced on the basis of terrigeneous minerals may be represented as follows (in descending order):

1. The upper garnet complex is subdivided into two horizons: the tourmaline-garnet and the rutile-garnet horizon. Lithologically, the complex is represented by anhydrite and gypsum and refers to the upper part of the gypsum-anhydrite facies (the upper portion of the middle complex, according to N. M. Strakhov).

2. The hornblende complex. Lithologically, it is represented by anhydrites (the lower part of Strakhov's middle complex) and halogen deposits (the upper part, according to Strakhov), sometimes facially replaced by terrigenous sediments (Allakaevo).

3. The lower garnet complex (sometimes containing scarce grains of common hornblende). Lithologically, the complex represents the lower part of the halogen deposits.

The attempts to correlate the sections of the Kungurian stage both in the territory of the Ishimbay area; and in the Karlino-Mrakov were successful.

In the Ishimbay area the over-massif sections of the Kungurian deposits were correlated to the depression deposits (Fig. 1). The over-massif rocks were found to be represented by the upper garnet complex and the upper part of the hornblende complex; while the lower portion of the hornblende complex and the lower garnet complex are characteristic of the rocks occurring in depressions (chiefly; the salt-bearing complex). Thus; the view is confirmed that the Kungurian deposits adjoin the slopes of the massifs; and do not envelop them. Hence; the sedimentation in the Kungurian time took place first in depressions; and later on; on massifs.

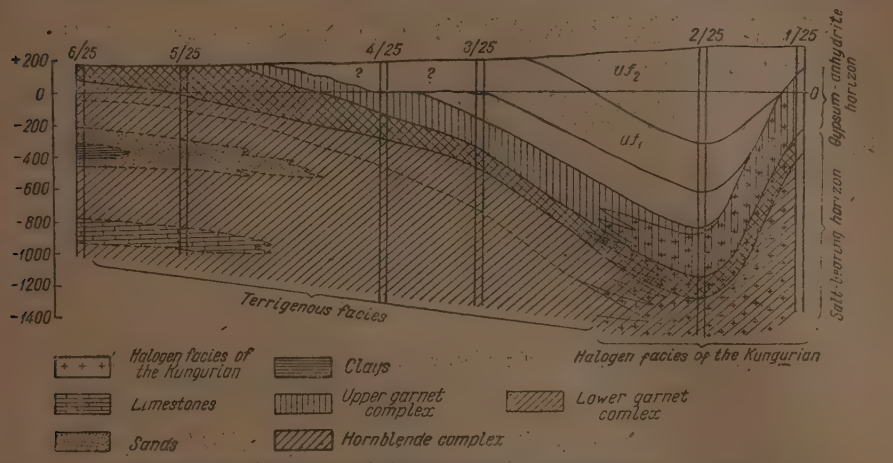

Fig. 2. Relation of terrigenous and halogen facies of the Kungurian in the Allakaevo section according to terrigenous minerals. Scale 1 : 20000

The Allakaevo section goes well to illustrate the possibility of replacement of the halogen deposits by terrigenous ones. The hornblende and the lower garnet complex are characteristic both of the halogen and of the terrigenous deposits of the Kungurian (Fig. 2).

In the Karlino-Mrakov region the works carried out by M. A. Sibert have confirmed the stratigraphy of the Kungurian deposits proposed by this author; it should be noted that in addition to the minerals recorded by the author, Sibert has noted the presence of volcanic glass and analcyme in the hornblende complex. The same results were arrived at by N. Z. Balitzkaya when studying the materials on the Kungurian of the Tatarian Sasykul.

In the Mrakov region prospectors attached great importance to platy anhydrites considered as a marker. Since in the North the platy anhydrites have been encountered at a great depth and in the South; at a lesser depth; it seemed as the Artinskian oil-bearing deposits rose from North to South. Mineralogical analyses have shown the platy anhydrites to be of no correlative value; since they belong to different mineralogical complexes. The horizons of the Kungurian, drawn according to mineralogical data, have shown, on the contrary, a «pitch» from North to South.

Natural exposures of the Kungurian of the near-Ural area of Bashkiria were also subjected to mineralogical study. The exposures may be subdivided into two groups: the first, embracing the Kungurian deposits at Smakayev, M. Baikov, Mashasha, Baigusino and Novo-Nikolaevka; and the second, to which belongs the Burlyuk gypsum, that of Mikhailovka on the Belaya River, and the Alexandrovsk on the Nugush River.

The first, northern group of exposures of the Kungurian stage is characterized by the upper garnet complex; *i. e.* belongs to the upper portion of the Kungurian.

The second, southern group is analogous to the northern, but is distinguished by the presence of scarce grains of hornblende and diopside. There are no reasons to question their simultaneous formation.

The presence of hornblendes and diopside is evidence of the beginning of a supply of clastic material to the southern basins. Thus; the first displacements on the Ural Range during the time of deposition of the upper parts of the Kungurian have in the first place affected the southern sections. It should be noted that the Ufa red stone deposits rest in different horizons on the Kungurian sediments. This is accounted for either by the absence of individual horizons of the Ufa series or by their presence at a certain depth, buried by the rising Kungurian deposits.

The mineralogical studies of the Kungurian deposits have brought us to the conclusion as to the necessity of using the method of correlative mineralogy in the solution of both practical and theoretical questions, related to the search-prospecting works in Bashkiria.

It should be hoped that the use of the method of correlative mineralogy, along with the study of the fauna of Kungurian deposits will enable us successfully to correlate the Kungurian deposits of the near-Ural region; which are so diversified from the lithological standpoint.

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Received
20.III. 1944.

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1944. Volume XLV, № 9

HISTOLOGY

AGE VARIATION OF SKIN IN KARAKUL LAMBS

By V. A. SHOLOHOV

(Communicated by L. A. Orbeli, Member of the Academy, 29.III.1944)

Several authors have been concerned with the skin structure of karakul sheep. But in their studies the age variations that take place in the skin of karakul lambs within the first days of their life have been paid scarcely any attention. It would be very interesting, however, to trace the changes in the histological structure of the skin which take place during this period, and to correlate them with the variations proceeding within the same period in the fleecy coat of the lamb.

The present work has been carried out with the purpose to trace the age variations in the histological structure of the skin of male karakul lambs during the first 30 days of their post-embryonic life, and their relation to the type of curl observable at that period of development.

Material and Technique. As material use was made of bits of skin excised from the sacral region of male lambs at the age of 1 to 31 days. The bits were fixed with 10 per cent formalin. The histological sections prepared from paraffin blocks were stained with Carazzi haematoxylin; with subsequent after-staining with a water-solution of eosin. 38 samples were taken at the pedigree Soviet farm «Kara-Kum»; Bukhara province, Uzbekistan; in spring 1942, from selected black karakul male lambs of vigorous constitution; in which the typical pattern of the fleece known by the name of «valek» (roll) was well-pronounced throughout the period of examination. Each day of development was represented by 1—2 samples.

Results. According to our data, the skin of a 1—3-day-old lamb consists of epidermis, corium and subcutaneous fat tissue. The epidermis is made up of two layers, the germinative and the corneous layers; the latter is frequently more or less desquamated and lies apart over the former one. The germinative layer consists of 2—3 layers of cells and contains at this age only a few pigment grains. The granular and the lucid layers are absent.

The corium, or the skin proper, is characterized by the absence in the upper part of the papillae which in most of animals are invaginated in the epithelium. The hair roots lie at a depth of $^2/_3$ of the corium and show a parallel arrangement. At the place where they pass into the hair bulb they form a slight kink in one direction; and in the upper part of the root a second kink in the opposite direction. The hair bulbs are situated at about the same level. The lower third of the corium, the reticular layer, which is made up mainly of collagenous fibres, passes without any marked transition into the underlying layer of subcutaneous adipose tissue. The sebaceous glands are situated at the level of the upper third of the corium. In this stage they are not yet ramified and have the shape of saccules. The bases of the sweat-glands are incorporated at the level of the hair bulbs. Their secretory

regions have the shape of small saccules with even walls; consisting of a single layer of glandular cells and of a layer of myoepithelial cells. The excretory ducts of the sweat-glands are straight and spirally wound at places; they start from secretory regions constricted in the shape of a funnel. The collagenous fibres reach their maximum development in the lower third of the corium underlying the hair bulbs, *i. e.* in its reticular layer. Their interlacing bunches are chiefly arranged in a horizontal direction.

As can be inferred from the examination of the histological sections, the texture of skin here described prevails in its main features throughout the period from the first day to the 30th day of development. During this period the typical parallel arrangement of the hair roots, characteristic of a regular, sterling curl «valek», is also stably preserved. The maintenance of a regular arrangement of the hair bulbs situated at the same level, and the parallel arrangement of the roots with an upper and a lower kink are probably responsible for the stability of the type of the curl pattern in the pedigree lambs throughout the period investigated.

Allowance being made for a definite range of variation, it is possible, however, to trace a general picture of the variations taking place in the skin of karakul lambs along with the general growth and development of the organism as a whole during the first month of their post-embryonic life. To these variations should in the first place be referred the quantitative changes in the separate components of the skin, which do not distort the general picture of their arrangement.

Beginning with the 7th day of life the epiderm begins to become thicker; the thickening proceeds at the expense of an increase in the number of cells which compose the germinative layer. In 1 and 2-day-old lambs the germinative layer consists of 2—3 strata of cells; towards the 15th day their number reaches 4, and finally, towards the 30 day, 4—5 layers. At the same time the pigmentation of the epidermis becomes more intense. In the epidermis of the skin of 1—2-day-old lambs but isolated pigment grains are observable within the field of vision; in 15-day-old lambs their number increases, and by the 30th day the accumulation of pigment grains may occasionally make the separate cell nuclei undistinguishable under the microscope. Only in isolated individuals a rather diffuse granular layer of the epidermis can be distinguished at an age of 15 days.

Data illustrating the variation in the thickness of epidermis are given in Table 1, column b.

Table 1

Age in days	Mean thickness of epidermis, in μ	Mean thickness of corium, in μ	Mean depth of bedding of hair-bulbs, in μ	Mean thickness of hair-bulbs, in μ	Average number of fluffy hairs per field of vision (under slight magnification)
a	b	c	d	e	f
1	19.2	2030	1192.5	116.8	4
7	20.4	2352	1660.0	169.6	—
10	—	—	—	—	7
15	22.2	2852	1820.0	170.4	—
19	—	—	—	—	8
20	—	2557	—	—	—
21	23.4	—	1750.0	176.8	—
23	—	—	—	—	—
31	27.0	2575	2132.5	189.6	9

As may be seen from Table 1, column c, the total thickness of the corium increases likewise.

Along with the total increase in thickness, the depth at which the hair roots are situated is also subject to variation, accompanied with a thickening of the hair-bulbs (Table 1, columns d and e).

During the first month of development of the lamb a gradual increase in the number of thin, fluffy hairs is observable; their roots are usually situated within the medium and the surface layers of the corium, above the main layer of thicker hairs (Table 1, column f).

The shape of the sebaceous glands remains unaltered, their depth of bedding shows no regular variation. Their size increases, however; and their total number per unit length does likewise (Table 2, columns b, c, d).

Table 2

Age in days	Mean depth of situaton of sebaceous glands, in μ	Mean length of sebaceous glands, in μ	Average number of sebaceous glands per each 5000 μ	Mean length of sweat-glands, in μ
a	b	c	d	e
1	222	287.5	7	477.5
7	150	312.0	7	535.0
17	192	350.0	7	—
19	—	—	—	562.5
23	185	375.0	8	—
31	197	325.0	10	615.0

The shape of the sweat-glands does not change appreciably either, although their size increases.

During the first month the arrangement of the corium fibres remains unaltered; along with the total thickening of the skin their bundles grow somewhat thicker.

Conclusions. 1. Age variation in the skin of karakul pedigree male lambs consists during the first month of their post-embryonic life chiefly in a gradual thickening of the skin and a proportional growth of all the components of the skin.

2. Within the first month the epidermis increases by 2—5 layers of cells. Along with this, the quantity of pigment in it is also found to increase.

3. By the end of the first month the sebaceous glands increase in volume and total number per unit area.

4. The sweat-glands retain throughout the first month their shape of oblong saccules; they increase in length without forming any coils; as observed in adult animals.

5. The number of fluffy hairs begins to increase since the 7th day of post-embryonic life.

6. The collagenous fibres of the corium become somewhat thicker, but their typical arrangement in the reticular layer remains unaltered.

7. The roots of the main hairs which are responsible for the peculiar pattern of the curl maintain their qualities throughout the first month of development. The arrangement of the hairs in the skin layer; typical of first-rate fleece of the type known by the name of «valek» (roll), is also maintained during this period, as well as the double kink of the hair-roots, which points to the elasticity of the hair.

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Received
29. III. 1944

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1944. Volume XLV, № 9

ENDOCRINOLOGY

FUNCTION OF THYROID AS DEPENDENT ON PITUITARY BODY ACTIVIZED BY LIGHT

By A. A. WOITKEWITSCH

(Communicated by L. A. Orbeli, Member of the Academy, 23.X.1944)

The existence of a functional relation between the thyroid and the anterior lobe of the pituitary body has been demonstrated experimentally on representatives of all classes of vertebrates. By administering to the animals the active principle of the pituitary gland it is possible to intensify the function of their thyroid. The removal of the anterior lobe is accompanied by underdevelopment or inhibition of the thyroidal apparatus.

Now what is then the agent affecting the thyrotropic functon of the anterior lobe of the pituitary body? It seems natural to assume that this agent is nothing else than light. Indeed, light is responsible for the changes that take place in the microstructure of the anterior lobe ([4],[8]). These changes seem to be accompanied by an increase in the supply of the gonadotropic hormone; for an artificial protraction of the light exposure applied every day was found to produce in a number of animals the activation of their sex cycle ([5], [6]). The present author has shown in an earlier paper that, along with gonadotropic hormone, thyrotropic hormone is likewise produced in the basophilic cells ([1], [2]). The assumption that light may possibly have a positive influence upon the thyrotropic function of the pituitary body appeared therefore to be well founded.

Indeed, the experiments carried out by the author went to confirm the correctness of this assumption ([3]). Frogs and toads were kept during various periods under contrasting light conditions (continuous illumination against dark). The pituitary glands of the experimental amphibians were examined histologically and tested for their content of thyrotropic hormone. The hypophysal tissue of such animals as had been exposed during 5—10 days to continuous illumination; was found to contain larger amounts of the active principle than that of animals withheld from light. According as the time of experiment was increased several times; the pituitary glands of the animals exposed to light were found to lose their thyrotropic properties to a considerable degree.

The conclusions as to the nature of the thyrotropic function of the anterior lobe and its relation to light exposure would much gain in significance were they based on the behaviour of the thyroid under varying conditions of the thyrotropic activity of the pituitary body, rather than on mere morphological investigations and biological tests of the hypophysal tissue.

The terrestrial turtle *Testudo horsfieldi* served as experimental material for this investigation. Similar to amphibians, these animals pass the winter under conditions precluding any possible influence of light. During the spring-summer season, light seems to play an essential part in their life activity. The experiments were carried on during spring and summer, in 1942, 1943 and 1944.

From among numerous experimental groups differing as to the length of light exposure we report in this place data for three groups; the results of which are the most illustrative (the length of exposure was 5, 12 and 35 days; respectively). Each group comprised, as a rule, two sets, composed of five turtles each. In one of the sets the animals were subjected to continuous illumination (from a bulb 400 W placed 50 cm above them), whereas the animals of the other set were withheld from light. In some of the cases there was a third set serving for comparison, which was kept under normal light conditions.

After the end of experiment the animals of all the sets were sacrificed without applying any narcosis. Small fragments of their pituitary lobes and thyroids were treated for histological examination, the bulk of the gland tissue was used for biological testing. Tadpoles of the species *Rana ridibunda* at a stage considerably prior to the setting-in of metamorphosis (hind limbs in the form of undifferentiated oval buds) served as test-objects. The homogeneity of the material (size and developmental stage) was attained by a careful selection of the tadpoles. To every tadpole was grafted a fragment of a gland, 1 mg by weight. As soon as the larvae within one of the sets displayed advanced metamorphosis, the observations were discontinued. The experimental sets, as well as the inoperated controls, were then sacrificed simultaneously. As indicators of metamorphosis; we took those larval organs as are subject to the most pronounced size variations because of resorption (tail and intestine).

The acceleration of metamorphosis is well illustrated by the figures denoting the difference between control and experiment; figures for each separate indicator, in per cent to control, are summarized in the table.

Graft	Time elapsed since start of experim., days	Sets	Indicators of metamorphosis			
			Body weight	Tail weight	Tail length	Intestine length
Pituitary body	5	Light	11.3	38.9	27.4	58.4
		Dark	5.6	13.2	7.4	40.9
	12	Light	9.6	27.6	16.6	49.1
		Dark	8.1	23.5	12.2	46.0
	35	Light	1.7	20.4	8.7	34.7
		Dark	7.8	38.9	12.6	51.2
Thyroid	5	Light	22.0	45.4	34.9	66.8
		Dark	25.3	54.0	43.1	72.6
	12	Light	7.0	24.3	11.2	29.0
		Dark	20.1	58.7	53.2	78.1
	35	Light	13.9	64.7	42.1	70.9
		Dark	8.8	51.9	37.2	67.2

Grafting with hypophysal tissue from turtles exposed to light during 5 days produced a much greater accelerating effect upon the process of metamorphosis than when the transplanted tissue was taken from animals kept in the dark during an equivalent period *. The pituitary lobes of illuminated animals contain more thyrotropic hormone than those taken from animals withheld from light. Variations have also been observed in the microstructure of the pituitary body: larger numbers of basophilic cells per unit area of section are observable in the pituitary bodies in the illuminated sets than in those kept in the dark. The effect of light is also to increase the size of the basophilic cells; their protoplasm is profusely granulated.

No important differences could be revealed in the structure and biological activity of the sets under comparison. A certain intensification in the function of the gland should, however, be pointed out for the illuminated set.

* The metamorphogenetic effect of the hormonal principle of the pituitary gland is transmitted through the activized thyroid only.

By increasing the expcsure two or three times no essential changes in the microstructure of the pituitary body could be attained. The biological activity of the gland is somewhat reduced thereby, but is is still superior to that recorded for the «dark» set. Within the same period changes typical of the state of hyperfunction take place both in the microscopic picture and biological activity of the thyroids. The epithelial cells of the follicles assume a cylindrical shape, th follicles of the thyroids are largely releaved of the colloidal substance they contained. The remaining colloid substance is vacuolized and stains but poorly. In the case of grafting with tissue of such glands the acceleration rate of metamorphosis (biological activity) is no important one. This should be taken to mean that a protraction of the period of exposure is accompanied by no further intensification of the secretory process; within the same period, however, the reflux of the thyrotropic hormone is enhanced considerably; owing to which the thyroid passes to the phase of hyperfunction.

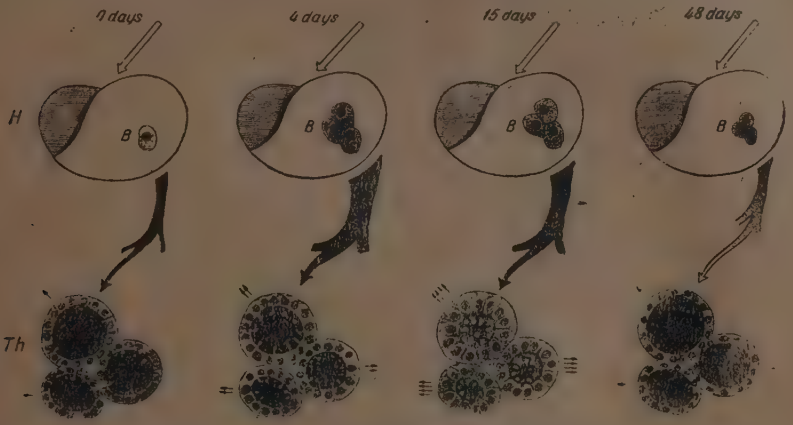
If the experiment is extended to a period of 35 days, the metamorphogenetic activity of the pituitary body decreases, which is evidence that the tissue of this gland became poor in the thyrotropic substance. Some morphological changes which had previously escaped our notice could now be observed: the total dimensions of the basophilic cells were reduced; the protoplasm became more compact, the granules vanished almost entirely. No appreciable change took place in the number of the cells. According to the state of the thyroid; one may believe that the concentration of the thyrotropic hormone in the blood has become lower, which would testify to a less intense reflux from the pituitary body. The biological activity of the thyroid is greatly increased because of the accumulation in the follicles of a large quantity of the chromophilic colloidal substance. It should be pointed out in this place that the transition of the thyroid to the state of «quiescence» may proceed, as shown by experiments involving the administration of the hypophysal hormone, even in such cases where the concentration of the thyrotropic hormone in the blood is during a rather long period maintained at a high level. This should not be taken to mean, of course, that in order to keep the function of the thyroid high, a certain concentration of the thyrotropic hormone need not be preserved up to a definite moment in the humoral medium. The data secured by us permit even of more far reaching conclusions.

Light is the agent whose presence guarantees for the work of the basophilic cells of the anterior lobe of the pituitary body. For the total of the basophilic cells which in certain animals are morphologically readily distinguishable from the rest of the structural elements of the anterior lobe, we suggest the name of «basophilic apparatus».

That the name can rightfully be applied to this complex of cells, may also be inferred from the fact that the group of hormones produced by the basophilic cells is endowed with a specific morphogenetic effect which is not peculiar to another type of the secretory cells, *viz.* the eosinophilic cells. Our experiments have demonstrated that the active substances localized in the basophilic or in the eosinophilic cells are morphogenetically antagonistic (2). The function of the basophilic cells, which is stimulated by light, does not seem to be confined to the production of the gonadotropic and thyrotropic hormones only, it comprises the whole complex of tropic hormones as well. In how far does the activation of the basophilic cells tell upon the function of other «receptory cells», cannot be made clear until further investigations have been made. The only assumption that can be hazarded at the time being is that the basophilic apparatus of the anterior lobe is producing a single active principle whose formation is controlled by light; rather than a whole complex of tropic hormones, as it is generally supposed. We have as yet no clear idea of what may possibly play the decisive part in the producing of the specific tropic effect, whether it is the concentration of the active substance, or the threshold of reaction of the gland's cells, which is not the same in different endocrine organs, or else the further transformation it undergoes in the humoral medium of the organism. The interaction between the «receptory glands» and their reciprocal

action upon the pituitary lobe cannot be left out of the account either, in so far as the elimination of the one gland is known to affect the efficiency of the tropic influence upon the glands.

An essential point in the efficiency of light is the «factor of length», or exposure time. A continuous illumination of the animals during a comparatively short period of time (1—3 days) was found to be accompanied by morphological and, consequently, also by functional alterations in the anterior lobe (7). The light received during the day cannot but tell upon the function of the pituitary body. The effect of light is to activize the production of the tropic principle in the basophilic apparatus of the gland. According as the period of illumination grows longer, the secretory function of the basophilic cells must also gradually rise up to a definite limit. The intensity of the evacuation of the hormone into the organism is also increasing along with it. If illumination is continued for a long



Basophilic apparatus of pituitary body as activized by light (scheme). *H*, pituitary body. *B*, basophilic apparatus. *Th*, thyroid follicles

time, the stable maintenance of the high intensity of secretion will necessarily lead to a functional exhaustion of the basophilic apparatus. The degree to which the pituitary body is enriched with the tropic substance decreases because of an uninterrupted elimination of the latter into the blood. The relation between the function of the pituitary gland and the thyroid, as affected by light, is schematically represented in the figure.

The formation of the active principle and its reflux from the gland are controlled by light. An exaggerate exposure to light brings about a functional exhaustion of the basophilic apparatus of the anterior lobe. The elimination of the light factor should, consequently, reduce or even arrest the secretion process and the process of evacuation, in particular. This must result in an accumulation of the active principle in the protoplasm of the basophilic cells and partly in the tissue of a given organ. In order to maintain a normal function of the pituitary body, *i.e.* to preserve a definite relation between the phases of secretion, the accumulation and evacuation of the hormonal principle, it is necessary that the periods of illumination alternate with the periods of darkness. Illumination must obey a definite rhythm, similar to that of the alternation of day and night, otherwise there can be no normal functioning of the basophilic apparatus; whose importance for the activity of the endocrine organs is a very high one. This makes us understand why seasonal variations in the relations between the diurnal and nocturnal periods are accompanied in certain vertebrates by the appearance and stimulation of cyclic processes determined by hormones.

The day-and-night rhythm and its seasonal modifications have served as the background which, along with other external factors, went to determine the nature

of a number of adaptations, formed at different stages of evolution of the organic kingdom. In the group which stands at the highest step of phylogenesis, the vertebrates, adaptation to the day-and-night rhythm has affected the most important link of the system which controls the most various functions of the organism.

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Received
1. X. 1944.

REFERENCES

[1] А. А. Войткевич, Бюлл. экспер. биол. и мед., III, № 3 (1937). [2] A. A. Woitkewitsch. C. R. Acad. Sci. USSR, XV, No. 6—7 (1937). [3] А. А. Войткевич, Бюлл. экспер. биол. и мед., XVII. № 6 (1944). [4] J. Benoit, Bull. biol. France et Belg., 71 (1937). [5] T. H. Bissonnette. Quart. Rev. Biol., 11 (1936). [5] W. M. Rowan. Biol. Rev., 13 (1938). [7] R. Sanchez, Salv. Virch. Arch., 300 (1937). [8] F. Stutinsky Bull. biol. France et Belg., 73 (1939).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1944. Volume XLV, № 9

ZOOLOGY

INDO-HIMALAYAN ELEMENT IN THE ORNITHOFAUNA OF RUSSIAN TURKESTAN

By K. A. VOROBIEV

(Communicated by L. A. Orbeli, Member of the Academy, 7.IV.1944)

As well-known, the ornithological fauna of Turkestan is of heterogeneous and rather complex composition. It represents all types of the Palaearctic, Siberian, European, Mediterranean, Mongolian, Thibetian, and Chinese fauna, among which the Mediterranean type is predominant. The high diversity and complexity of the Turkestanian ornithofauna is due, aside from the physical-geographical and climatic conditions, and the variety and abrupt changes in the landscapes, largely to the history of its formation.

Turkestan seems to have been the area of displacement and migration of numerous faunistic elements which have supplemented and modified its ancient complex, the latter consisted chiefly of forms of arid and steppe character. Suffice to say that we can meet in Turkestan representatives of such remote faunistic elements as, for example, *Aegolius funereus*, *Surnia ulula*, *Picoides tridactylus*, *Nucifraga caryocatactes*, *Loxia curvirostra*, *Turdus atrogularis*, *Prunella atrogularis* (Central Tien-Shan), and *Acridotheres tristis*, *Terpsiphone paradisi*, *Chaimarrornis leucocephala*, *Microcichla scouleri*, *Garrulax lineatus*, *Hirundo smithi* and many others, in the South of Tadjikistan. The penetration to Central Asia of typical north-tayga species, on the one hand, and of Indo-Himalayan species, on the other, go well to illustrate the heterogeneity and complexity of the genesis of the Turkestanian ornithofauna.

It is noteworthy that some of the tayga-species, say, *Nucifraga caryocatactes*, *Loxia curvirostra*, *Turdus atrogularis* and *Prunella atrogularis*, extend still farther South, and occur in the Himalayan Mountains (1) along with southern forms of the Chinese ornithofauna, occupying but different biotopes.

An analysis of the Turkestanian ornithofauna makes it evident that, contrary to the opinion generally adopted, Indo-Himalayan species represent in Turkestan a very extensive, well-differentiated group, although their area of distribution is often a very limited one. We refer to this group the following 28 species*: *Falco jugger*, *Porphyrio poliocephalus*, *Lobivanellus indicus*, *Streptopelia cambayensis*, *Picus squamatus*, *Corvus levaillantii*, *Acridotheres tristis*, *Mycerobas carnipes*, *Erythrina rhodochlamys*, *Emberiza stewarti*, *Certhia himalayana*, *Parus rufonuchalis*, *Leptopoecile sophiae*, *Lanius vittatus*, *Lanius schach*, *Terpsiphone paradisi*, *Muscicapa ruficauda*, *Puylloscopus occipitalis*, *Phylloscopus griseolus*, *Garrulax*

* As to *Melpastes leucogenys*, *Phylloscopus subviridis* and *Chaimarrornis fuliginosa*, reported by N. A. Zarudny from Bukhara (2), we do not find it possible to include them into the composition of the ornithofauna of Russian Turkestan for lack of collectional specimens available

lineatus, *Myophonus coeruleus*, *Saxicola caprata*, *Adelura coeruleocephala*, *Chaimarrornis leucocephala*, *Calliope pectoralis*, *Microcichla scouleri*, *Hirundo smithi*, *Riparia paludicola*.

As should have been anticipated, considerable part of the Indo-Himalayan elements listed above are concentrated in Tadjikistan. Both in its mountainous parts and in the plain, we encounter 24 species of the whole complex of the Indo-Himalayan forms penetrating to the territory of the Russian Turkestan. Thus, four species only, *viz. Porphyrio poliocephalus*, *Lobivanellus indicus*, *Picus squamatus* and *Lanius vittatus*, are missing in Tadjikistan. Farther North-East, within the Tian-Shan system, there occur also *Streptopelia cambayensis*, *Mycerobas carnipes*, *Erythrina rhodochlamys*, *Emberiza stewarti*, *Certhia himalayana*, *Parus rufonuchalis*, *Leptopoecile sophiae*, *Lanius schach*, *Terpsiphone paradisi*, *Muscicapa ruficauda*, *Phylloscopus occipitalis*, *Phylloscopus griseolus*, *Myophonus coeruleus*, *Adelura coeruleocephala*, *Calliope pectoralis*, *Microcichla scouleri*.

Individual species of Indo-Himalayan fauna penetrates till farther northward, thus, for example, *Emberiza stewarti* is encountered in the mounts of Kara-tau, *Lanius schach* is spread up to the lower reaches of the Syr-Daria river, *Streptopelia cambayensis* and *Saxicola caprata*, down to the lower reaches of the Amu-Daria, while *Mycerobas carnipes*, *Erythrina rhodochlamys* and *Phylloscopus griseolus* attain Tarbagatai, the latter species penetrating still farther North-East, up to the Altay. No more than five Indo-Himalayan species penetrate to the arid region of south-eastern Turkmenia, these are *Lobivanellus indicus*, *Streptopelia cambayensis*, *Picus squamatus*, *Lanius vittatus* and *Saxicola caprata*, out of which *Lobivanellus indicus*, *Picus squamatus** and *Lanius vittatus* are encountered solely in this part of the territory of Russian Turkestan.

In the mountains of Kopet-Dag, as well as in the Great Balkhan mountains, a single species out of the representatives of the Indo-Himalayan ornithofauna is encountered, *viz. Mycerobas carnipes*. This species is widespread in the mountains of Central Asia, extending from the Great Balkhan mountains to the Tarbagatai in the East. Only one of the Indian species is found to penetrate down to the lower reach of the Atrek River, and this is *Porphyrio poliocephalus*.

It is of interest to note that, according to Zarudny ([4], [5]), nine Indo-Himalayan species out of the number of species occurring in Central Asia, are supposed to nest in north-eastern Iran. These species are as follows: *Porphyrio poliocephalus*, *Lobivanellus indicus*, *Streptopelia cambayensis*, *Picus squamatus*, *Acridotheres tristis*, *Mycerobas carnipes*, *Lanius vittatus*, *Myophonus coeruleus* and *Saxicola caprata*.

Two contradictory opinions are to be found in the literature dealing with the origin of the Indo-Himalayan element of the ornithological fauna of Turkestan. Mensbir ([6]) and Serebrovsky ([7]) believe the Indo-Himalayan species to be the most ancient elements of the Turkestanian fauna; their chief argument is that most of these species here gave rise to new forms. Unlike them, Dementiev ([8]) considers this complex of southern species not as the relicts of an ancient fauna, but as the latest stratifications of the Turkestanian fauna, which have penetrated there during a rather recent time.

We are inclined to view the problem at a different angle, which enables us to reconciliate the two antipodal opinions advanced by earlier investigators. A detailed examination of the abundant material both from the territory of Russian Turkestan and of India, as well as an analysis of the species available, made us conclude that the different species of the southern complex played a different rôle in the formation of the modern ornithofauna of Turkestan. It should always be kept in mind that the Indo-Himalayan complex embraces most diversified taxonomic groups and species of absolutely different ecological lability, which inhabit zones characterized by most diversified landscapes. Consequently, it can

* N. A. Bobrinskoy ([3]) reports from the Kopet-Dag mountains *Picus squamatus*. But this is a mere error, for this pie is not to be found anywhere in the mountains of Kopet-Dag.

be assumed *a priori* that the appearance of different species of the Indo-Himalayan complex in Central Asia was undoubtedly different and took place at different historical epochs. Some of them may, indeed, be nothing else than ancient relicts while others are undoubtedly representatives of a recent, subsequent strata in the fauna of Turkestan. A considerable number of species (*Picus squamatus gorii*; *Certhia himalayana taeniura*, *Calliope pectoralis ballioni*) assumed here an intense expression, peculiar geographical forms, which is evidence of their relatively ancient origin; others are absolutely identical with the Indian species (*Acridotheres tristis tristis*, *Mycerobas carnipes speculigerus*, *Parus rufonuchalis rufonuchalis*; *Muscicapa ruficauda*, *Microcichla scouleri*), which may possibly be accounted for by their poor lability; finally, some of the species have but quite recently penetrated to the territory of Central Asia and proceed in extending their area of distribution. A classical example of such a migration of a species farther north is offered by *Acridotheres tristis* which was never found in Russian Turkestan until 1907. At the present time the area of nesting of the Indian mayna embraces the valley of the Amu-Daria river, from the mouth of Kafirnigan to Deynau (40 km north of Charjuy). In southern Uzbekistan and the south-western parts of Tadjikistan this species has occasionally penetrated to the southern piedmonts of the Gissar mountain ridge.

In spring 1939 I happened to find considerable numbers of Indian maynas nesting in the valley of the Amu-Daria River, in the region of the station Charshang (south-eastern Turkmenia). They were also of rather common occurrence in Karljuk.

Deeper in the mountains I encountered these birds again (70 km north of the Amu-Daria). It is of interest that according to information obtained from local people, the maynas appeared in Karljuk and Kuguitang after 1933. This information is in full agreement with literary data on the migration of this species during the recent years.

Another illustrative example of the extension of the area of distribution in Central Asia is offered by the species *Streptopelia cambayensis*. This species extends both in the western and eastern direction; it is not until the last decades that it has penetrated from the valley of the Amu-Daria to the region of Ashkhabad, where this turtle-dove was unknown at the time of the first expeditions of Zarudny (⁹) to the Transcaspian region (1884—1892). The westernmost point of occurrence of *Streptopelia cambayensis* in Turkestan is actually the station Besmein, in the region of Ashkhabad. It is to be pointed out that this species has not yet penetrated either to Kizyl-Arvat, or the region of Kara-Kala (1940), although this region abounds in arboreal growths stimulating the nesting of this species. As to the distribution of *Streptopelia cambayensis* eastwards, the species extends in Semirechie up to Karabulak in the western spurs of the Jungar Alatau. Among this group of birds which are now in the state of migration may also possibly be classed *Lanius vittatus*; these birds have not been found in Russian Turkestan until 1936 (Agar-Cheshme, East of the upper reaches of Tejen); in the next year they were encountered in the region of Kushka. This supposition is the more plausible as the two regions have been explored by Zarudny at the time of his expeditions.

It is a fact of general knowledge that the more readily a given species becomes adapted to diversified, often rather complicated environmental conditions, the greater is the ease with which it extends beyond the boundaries of its area of distribution. Among the Indo-Himalayan group as ecologically plastic species may be considered *Emberiza stewarti* which, according to Meinertzhagen (¹⁰); inhabits arboreal growths in the western Himalayan, whereas in Iran, Afganistan and Russian Central Asia it is found on the slopes of absolutely naked and desert mountains, devoid of any arboreal growth whatever.

Dementiev (¹¹) classes among the species actually migrating to Central Asia also *Myophonus coeruleus*. According to this author, we are perhaps facing here the migration of this bird northward, for it has never been discovered by A. N. Sewertzoff, and this bird, of large size and endowed with an extremely loud voice, could not possibly be overlooked of by this explorer. Without denying the possibility of

an actual migration of *Myophonus coeruleus*, it should, however, be pointed out that A. N. Sewertzoff ([12]) has by no means overlooked this bird in the Tian-Shan mountains, for he mentioned it more than once in his classical work on the vertical and horizontal distribution of Turkestan fauna.

Received
7. IV. 1944.

REFERENCES

[1] E. C. Stuart Baker, The Fauna of British India, Birds, vol. I—VIII, 1922—1930. [2] Н. А. Зарудный, Орнитологический вестник, № 2 (1910); № 1 (1912). [3] Н. А. Бобринской, Животные и природа СССР, Географич. распространение наземных позвоночных, 1938. [4] Н. А. Зарудный, Зап. Русск. геогр. о-ва, XXXVI (1903). [5] Н. А. Зарудный, там же, L (1916). [6] М. А. Мензбир, Зоологич. участки Туркестанского края и вероятное происхождение фауны последнего, 1914. [7] П. В. Серебровский, История животного мира СССР, 1935. [8] Г. П. Дементьев, Бюлл. Моск. об-ва испытат. природы, XLVII (1939). [9] Н. А. Зарудный, Орнитологич. фауна Закаспийского края, 1896. [10] Meinertzhagen, The Ibis, No. 3—4 (1938). [11] С. А. Бутурлин и Г. П. Дементьев, Птицы СССР, IV, 1937. [12] А. Н. Северцов, Вертикальное и горизонтальное распределение туркестанских животных, 1873.

Prix $ 0.50